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with  
Responsive Functions**

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**2000**

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Kyoto University**

## Preface

The studies presented in this thesis have been carried out under the direction of Professor Yoshiki Chujo at Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University during 1995 ~ 2000. The studies are concerned with the investigation of organic-inorganic polymer hybrids prepared from field-responsive polymers.

The author wishes to express his sincerest gratitude to Professor Yoshiki Chujo for his constant guidance, valuable suggestions, and warm encouragement throughout this work. The author is deeply grateful to Mr. Naoki Yoshida, Mr. Kaoru Adachi, Mr. Hideaki Itoh, and Mr. Tomoki Ogoshi for their great contribution to this work. The author also wishes to state his appreciation to Dr. Kensuke Naka, Dr. Chilukuri Ver Avadhani, Dr. Ryo Tamaki, Dr. Toshiyuki Oyama, Mr. Yoshikuni Sasaki, Dr. Noriyoshi Matsumi, Dr. Gen-ichi Konishi, and Mr. Kenji Komori for valuable discussions during the course of the study. The author is also grateful to Mr. Takuya Horiguchi, Mr. Mitsuo Yaguchi, Mr. Ken Samura, Mr. Mao Yamaguchi, Mr. Kyung-Min Kim, and all his colleagues for their active collaboration.

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Finally, the author wishes to show his deep appreciation to his family, especially his parents, Mr. Toshio Imai and Mrs. Noriko Imai for their continuous assistance and encouragement.

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February 2000

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General Introduction



## General Introduction

### Organic-Inorganic Nanocomposites

#### *Composite Materials*

Combination of different types of monolithic materials (organic, inorganic, metallic) has been an effective way to achieve the desired properties which are not able to be accomplished with a single material. From the beginning of the commercial production of plastics and rubbers, fiber reinforcements or fillers were combined to improve mechanical strength, stiffness, thermal stability, dimensional stability, and other properties.<sup>1,2</sup> The reinforcing agent can be made of organic, inorganic, metallic, or ceramic materials. These kinds of classical composites are combinations of materials differing in composition or form on a macroscopic ( $> \mu\text{m}$ ) scale. All of the constituents in the composite retain their identities. Additivity of the properties of each component, usually complementally, determines the properties of composites. The shape and orientation of matrix and disperse phase, and specific interaction in the interface region are also important.

#### *Nanocomposite Materials*

Recent advances in the development of nanocomposites or hybrid materials opened a new horizon in the field of materials science.<sup>3,4</sup> Here the word "nanocomposites" or "hybrids" describes composites where at least one of the components possesses a dimension less than several nanometers. Further reduction in the domain size results in "molecular composites". As the greater part of dispersed phase is in the interfacial region, enhanced effect of the interface, for instance, unusual reinforcing effect, can be observed.<sup>5-8</sup> Sometimes the characteristics of the constituent in the size of nanometer are different from those in bulk, resulting in unique materials.<sup>9-11</sup>

One of the most striking feature of the hybrid materials is optical transparency. Due

to dispersion of components in the order of nanometers, which is far less than the wavelength of visible light and even near ultraviolet light, scattering loss is avoided.<sup>12</sup> Application of these materials to optics is particularly promising.

### Sol-Gel Derived Hybrid Materials

Sol-gel technique is quite versatile to prepare such hybrid materials.<sup>13</sup> It is possible to prepare inorganic oxides at ambient temperature by polymerization and coagulation of metal and semimetal hydroxides or of their organic ethers (alkoxides) or esters. The most typical example is the formation of silica gel from silicon alkoxide (Scheme 1).



**Scheme 1.** Sol-gel reaction of alkoxysilanes.

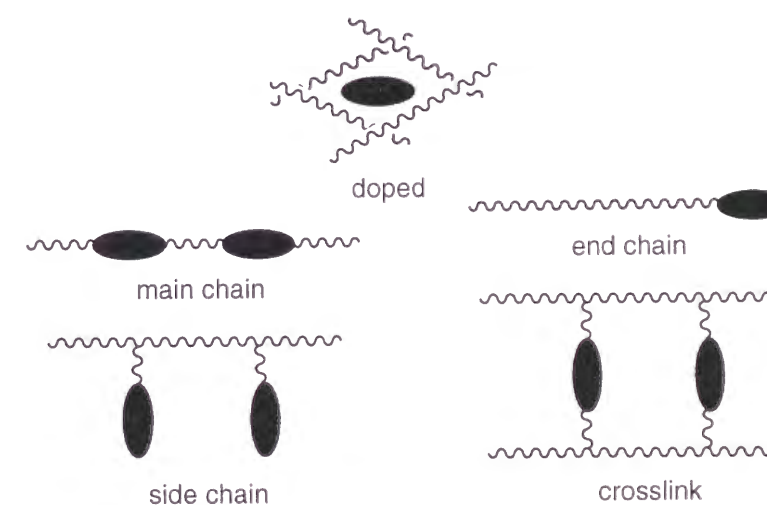
The reaction proceeds at ambient temperature from the starting homogeneous solution to sol, wet gel, and xerogel (dry gel) after evaporation of the solvent. The structure of the obtained silica gel is influenced by various parameters such as reaction temperature, solvent, pressure, amounts of water, as well as the catalysts employed. To obtain dense or crystal phase of ceramics, heating at higher temperature is generally required.

Since silica xerogels can be obtained without heating to high temperature, organic modification of silica gel matrix is also achieved through the sol-gel processing without degradation of organic residues. As Si-C bond is stable to hydrolysis, alkyl or aryl residues could be incorporated into silica matrix with alkyl- or aryl-substituted alkoxysilanes.<sup>14-16</sup> Precursors such as 3-methacryloxypropyltrialkoxysilane or 3-glycidoxypropyltrialkoxysilane are capable of polymerizing both at alkoxysilyl group via sol-gel reaction and at methacryl or glycidyl groups via radical polymerization or polycondensation.<sup>14,15,17-22</sup> These multifunctional

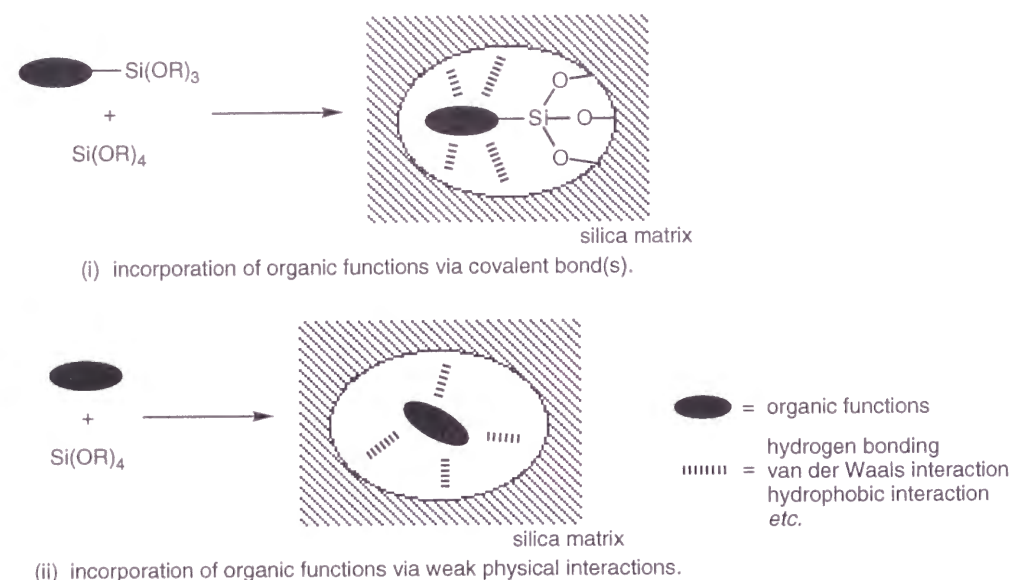
precursors afford the other preparative method of hybrid materials of organic polymers and silica gels. Prepolymers can be incorporated via covalent bond<sup>17-22</sup> or only with physical interactions such as hydrogen bonding.<sup>17-33</sup> Impregnation of methyl methacrylate (MMA) to porous silica xerogel and subsequent radical polymerization of MMA give nanocomposites which are quite suitable for photonics applications.<sup>34</sup> These materials are very promising by themselves as contact lenses,<sup>35</sup> optical waveguides,<sup>36,37</sup> hard coatings and diffusion barriers,<sup>15</sup> gas separation membranes,<sup>38</sup> and many others.

### Amorphous Solids as Host Matrices for Functional Molecules

Organic polymers and sol-gel derived silica gels have been utilized as the host matrices for a wide variety of functional molecules.<sup>39-52</sup> The organic-inorganic hybrid materials are expected as the third candidate for host matrices which offer improved characteristics. Organic functions can be integrated either through covalent bonding or by physical entrapment. Covalent incorporation of functional molecules into organic polymers might be possible in the main chain, in the side chain, at the end, through crosslinking, and so forth (Scheme 2). In the case of sol-gel glasses, organic functions having alkoxysilyl group can be utilized (Scheme 3).



**Scheme 2.** Incorporation of functional molecules into organic polymers.



**Scheme 3.** Integration of organic functions into silica gel via sol-gel process.

Incorporation of functional groups into organic-inorganic hybrid matrices is accomplished by the combination of above methods. Since the pioneering work of the introduction of laser dye (Rhodamine 6G) in silica gel by Avnir *et al.*,<sup>53</sup> much efforts have been done on the encapsulation of functional molecules in sol-gel derived matrices. UV-vis dyes lasers,<sup>53-57</sup> near-IR dyes lasers,<sup>58,59</sup> nonlinear optical materials,<sup>60-68</sup> photochromic chromophores,<sup>69-71</sup> chemical and biochemical sensors,<sup>51,52,72-74</sup> catalysts,<sup>75-77</sup> as well as liquid crystals<sup>78,79</sup> have been incorporated in these matrices.

Investigations on the nature of the organic-inorganic hybrid materials as host media were also carried out.<sup>80-83</sup> The nature of the local microenvironment surrounding the entrapped molecules is usually decisive to achieve the desired property. It is necessary to understand the microenvironment around the doped molecules to predict and design the property of the entrapped molecules and the resulting characteristics of the materials. In the case of organic-inorganic hybrids, the situation is quite complicated since the location of the molecule might be organic phase, inorganic phase, or interface region. Luminescent chromophores were known to be powerful tools to study the microenvironment of solid systems (e.g., local free

volume, microscopic viscosity, polarity of microenvironment).<sup>39,40</sup> Isomerization behavior of photochromic materials can be considered as another probe.<sup>42</sup>

## Polymeric Responsive Materials.

### Polymers Responsive to Stimulation

Research and development of organic polymers that possess responsive properties to a certain stimulation are very exciting.<sup>84</sup> Due to the advantages of polymeric materials, that is, high flexibility, high processability, versatility in design of chemical structure and large variety of functionality, they possess technological importance as well as a scientific fascination. Various kinds of stimulation can be applied; light, heat, electricity, chemical environment (pH, humidity, *etc.*), specific chemical species (ions, bioactive molecules, *etc.*), mechanical stress, and magnetic fields.

It is possible to classify these materials into two categories based on *reversibility*. *Irreversible* change of properties by imposition of stimulus is widely utilized for negative- or positive-photoresists, photocuring of coatings, photo- or biodegradable polymers, and so on.<sup>40</sup> *Reversible* conversion of properties can potentially be applied into devices as novel intelligent materials with sensing, processing, and actuating functions.<sup>40,42,84,85</sup> *Reversible* materials are the main objects in this thesis.

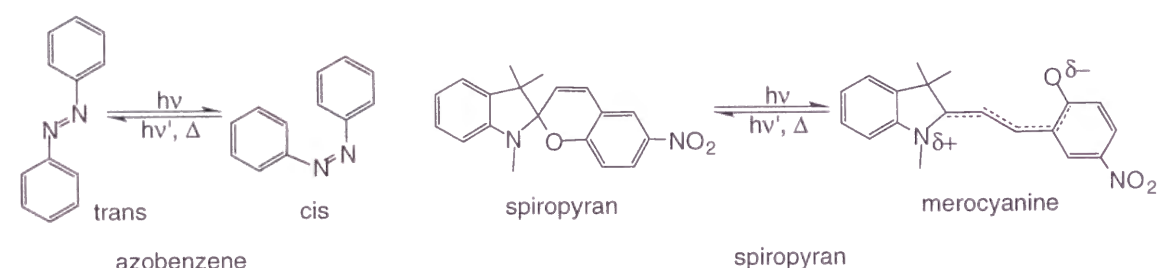
### Photochromic Materials

Materials responsive to light (electromagnetic radiation) are called *photoresponsive* materials. Representative example of such materials is *photochromic* materials.<sup>42</sup> Photochromism is defined as a reversible transformation of a single chemical species between two states having different distinguishable absorption spectra, such a change being induced in at least one direction by the action of light. In organic compounds, photochromism is related to the following structural modifications:



- (i) cis-trans isomerization,
- (ii) pericyclic reaction (ring-opening/ring-closure),
- (iii) tautomerism (hydrogen transfer),
- (iv) dissociation process.

Azobenzene (cis-trans isomerization) and spiropyran (ring-opening/ring-closure) are the most typical photochromic compounds (Scheme 4). Basically, the irradiation of ultraviolet light causes the transformation from thermally stable *trans*-azobenzene or spiropyran (closed form) to less stable *cis*-azobenzene or merocyanine (opened form). The reverse reaction takes place both thermally or by the irradiation of visible (longer wavelength) light.



**Scheme 4.** Photochromic compounds.

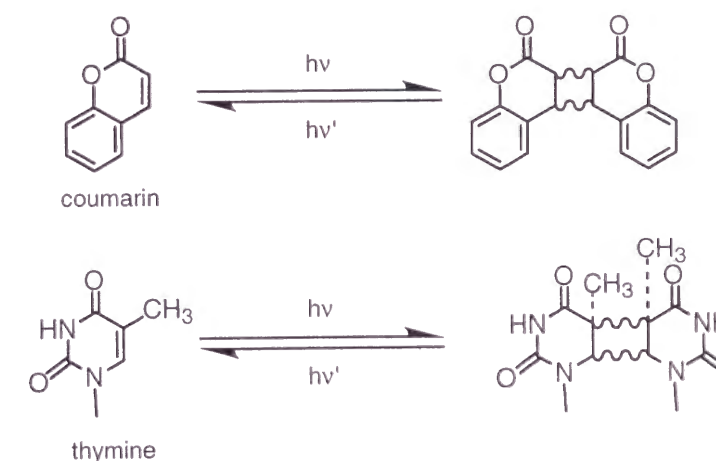
Optical switches and optical recording media based on photochromism have been developed. Natansohn *et al.* proposed the information storage system based on the orientation of azobenzene chromophore in polymer films induced by the irradiation of linearly polarized light.<sup>86</sup> Photochromic dyes having improved properties suitable for memory applications have been synthesized. They should satisfy many requirements such as thermal irreversibility, high fatigue resistant property, fast response, nondestructive reading property, and so forth. One of the best candidates is diarylethenes developed by Irie *et al.*<sup>87</sup>

Photochromic transformation of structure not only induces the change in the absorption spectra but in the emission spectra, refractive index, and dielectric constant. These modifications other than color changes are intrinsic in photochromic phenomena and thus offer broader prospects for practical applications of photochromic compounds. The reversible transformations

in molecular levels induce conformational changes of matrix molecules surrounding the photochromic molecule. Thus photochromic molecules can trigger subsequent rearrangement of microenvironments and lead to a variety of modifications of physical as well as chemical property of the system. Orientation of liquid crystalline materials is controlled by self-assembled monolayer of azobenzene derivatives (command surface).<sup>88,89</sup> Photoisomerization of azobenzenes and spiropyrans attached covalently to polymers leads to the change of solubility,<sup>90</sup> cation binding capability,<sup>91</sup> swelling behavior<sup>92</sup> of polymers. Photoinduced dimensional change of polymer chains has also been achieved.<sup>93</sup>

#### Reversible Cycloaddition

Some kinds of *intermolecular* reactions are *reversible*, that is, the bond-formation and the reverse cleavage reaction occur efficiently and the processes can easily be controlled with moderate conditions. It is well known that the disulfide (e.g., cysteine residue of the protein) can be ruptured by reduction to form two thiol groups, and the S-S bond is reformed by mild oxidation.<sup>94</sup> *Pericyclic* reactions, for instance, photochemical  $[2\pi+2\pi]$  cycloadditions and thermal  $[2\pi+4\pi]$  cyclization (so-called Diels-Alder reactions), are other representatives.<sup>95</sup>

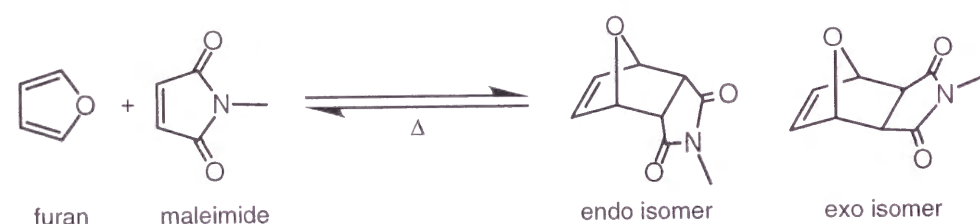


**Scheme 5.** Photocycloaddition reaction of coumarin and thymine.

Many double-bond compounds undergo  $[2\pi+2\pi]$  cycloaddition reactions when

photochemically excited. Coumarins photodimerize and form cyclobutane ring by the irradiation with the light longer than 310 nm.<sup>96</sup> When thymine (pyrimidine base which is an element of DNA) is UV irradiated, the photocyclization occurs.<sup>97</sup> This reaction is considered to be a cause of mutagenesis in DNA. Each photodimer in general has four stereoisomers. The reverse reaction (photocleavage of cyclobutane ring) is promoted by the light of shorter wavelength. This type of reaction has been utilized for the formation of oligomers and polymers,<sup>98</sup> reversible photomemory in polymers,<sup>99</sup> and generation of uniaxial planar alignment of adjacent liquid crystal polymer layers by linearly polarized light.<sup>100</sup>

In the Diels-Alder reaction, a six-membered ring is produced by  $2\pi+4\pi$  cyclization of a double bond (dienophile) and a conjugated diene.<sup>95</sup> Contrary to  $2\pi+2\pi$  system, this reaction generally takes place thermally. Reverse reaction, or often designated as *retro*-Diels-Alder reaction, can be simply carried out by heating.



**Scheme 6.** Diels-Alder reaction between maleimide (dienophile) and furan (diene).

The intermolecular bond formation reactions between the side chain of polymers result in crosslinking and thus the construction of polymer gels. Functional gels responsive to stimulation have been designed.<sup>101-107</sup>

### Responsive Polymer Gels

Some polymers and gels show reversible phase transitions in response to changes in temperature, solvent composition, pH, and electric field.<sup>85</sup> The most typical example which is responsive to temperature change is poly(*N*-isopropylacrylamide) (PNIPA).<sup>85,108</sup> PNIPA precipitates from water solution above a critical temperature around 32 °C, called lower

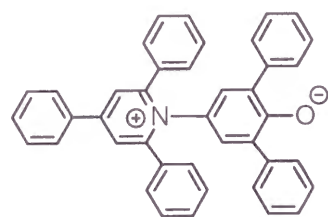
critical solution temperature (LCST), and dissolves below LCST. This is due to the hydrophobic interaction between NIPA and water molecules. When it is crosslinked, the obtained hydrogel collapses above LCST, while it swells and expands below LCST. The change is discontinuous. These materials have become of major interest as novel intelligent materials such as artificial organs and drug delivery systems.

### Solvent (Matrix) Polarity

It is widely recognized that rates and equilibrium positions of chemical reactions, as well as absorption bands in UV/vis/near-IR, IR, NMR, and ESR spectroscopies, are intrinsically affected by the surroundings of the chemical species, namely, solvents or matrices.<sup>109</sup> Much efforts have been dedicated to understand solvent effects on chemical reactions in terms of the so-called *solvent polarity*. Though it is not easy to define and to express quantitatively, it seems favorable to define "solvent polarity" simply as the overall solvation capability (or solvation power) of solvents.<sup>109</sup> Namely, it depends on the action of all possible, specific and nonspecific, intermolecular interactions between solute ions or molecules and solvent molecules. Those interactions leading to definite chemical alterations of the solutes (such as protonation, oxidation, reduction, chemical complex formation) are excluded.

Neither quantitative description of the "solvent polarity" thus defined by single physical solvent parameters such as dielectric constants and dipole moments nor reliable theoretical expressions for the prediction of solvent effects are possible. Therefore the introduction of empirical parameters of solvent polarity was attempted. A common approach is to assume that some particular reaction rate, equilibrium, or spectral absorption is a suitable model for a large class of other solvent-dependent processes. Dimroth and Reichardt have proposed a solvent polarity parameter,  $E_T(30)$ ,<sup>110</sup> based on the transition energy for the longest wavelength solvatochromic absorption band of the pyridinium *N*-phenolate betaine dye (Scheme 7).





**Scheme 7.** Pyridinium *N*-phenolate betaine dye for  $E_T(30)$  scale.

This compound shows one of the largest negative solvatochromism, that is, very sensitive probe, and the  $E_T(30)$ -value for a solvent is simply defined as the transition energy of the dissolved betaine dye measured in kcal/mol (eq. 1).

$$E_T \text{ (kcal mol}^{-1}\text{)} = hcN_A \nu_{\max} = 28,591/\lambda_{\max} \text{ (nm)} \quad (\text{eq. 1})$$

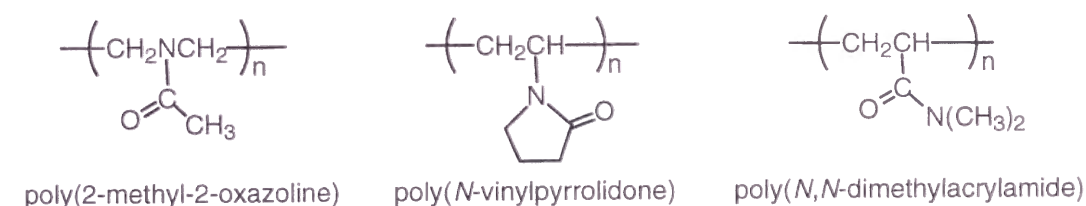
Here  $h$  is Plank's constant,  $c$  is the speed of light in a vacuum,  $N_A$  is Avogadro's number, and  $\nu_{\max}$  and  $\lambda_{\max}$  are the frequency and the wavelength of the absorption maximum of the intramolecular charge-transfer band of the dye. A high  $E_T$  value corresponds to high solvent polarity.  $E_T(30)$ -values have been determined for more than 360 pure organic solvents and for a great number of binary solvent mixtures.<sup>111</sup> In general, the  $E_T(30)$ -values exhibit a good, mostly linear correlation with a large number of other solvent-sensitive processes. This dye is not only sensitive to changes in solvent polarity, but also to changes in temperature, pressure, as well as on the addition of electrolytes.<sup>112</sup>

### Background and Survey of the Present Work

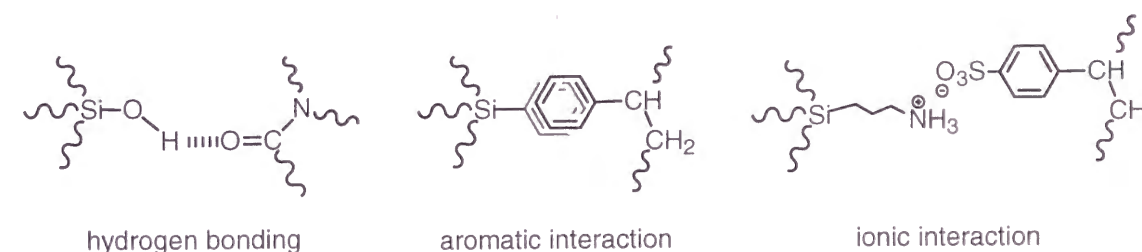
Prof. Chujo's group has been interested in the development of novel organic-inorganic polymer hybrids by utilizing the sol-gel technique.<sup>23,24</sup> Main focus is to create the organic-inorganic polymer hybrids without covalent bonding between organic and inorganic components.

As shown in Scheme 1, silanol groups are generated during the sol-gel reaction of

alkoxysilanes under acidic condition. The hydrogen bonding interaction with these silanol groups and organic polymers is a key to achieve homogeneous dispersion. Organic polymers having strong hydrogen acceptor groups such as amide group could be incorporated into silica gel at a molecular level. Thus transparent and homogeneous polymer hybrids were obtained from poly(2-methyl-2-oxazoline), poly(*N*-vinylpyrrolidone), and poly(*N,N*-dimethylacrylamide) (Scheme 8). The formation of hydrogen bonding between the amide groups and the silanols (Scheme 9) was confirmed by FT-IR spectroscopy. The vibration peak of amide carbonyl group was found to shift to lower wavelength. The homogeneity of these polymer hybrids was verified by nitrogen adsorption porosimetry as well as atomic force microscopy and it was found that the size of the domain is smaller than a few nanometers.



**Scheme 8.** Chemical structure of amide containing polymers.

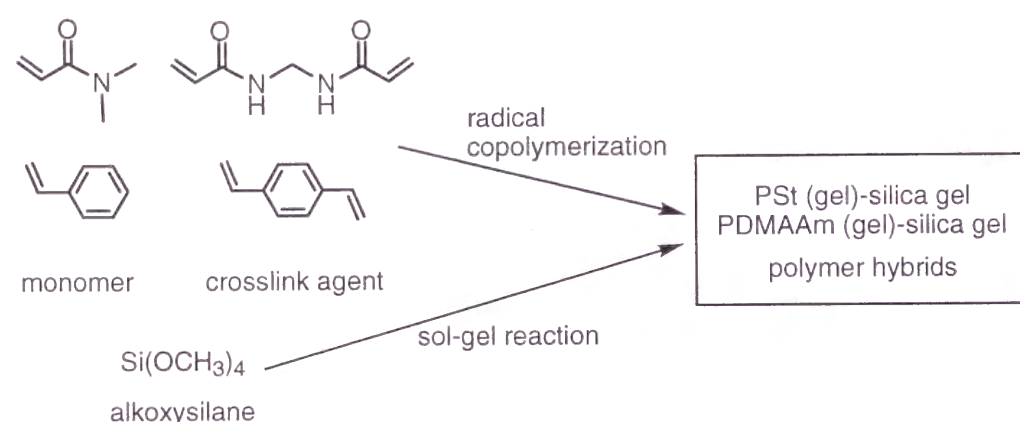


**Scheme 9.** Interactions between organic and inorganic components.

Other interactions such as the aromatic interaction<sup>29-31</sup> and the ionic interaction<sup>33</sup> could also be utilized to achieve homogeneous polymer hybrids (Scheme 9). Polymer hybrids from hydrophobic polystyrenes or poly(diallyl phthalate) were successfully obtained.

Simultaneous *in-situ* chemical reactions of organic components afford the other type of polymer hybrids. Acidic hydrolysis of ester groups of poly(vinyl acetate) during the sol-gel reaction gave homogeneous polymer hybrids of poly(vinyl alcohol) and silica gel.<sup>114</sup>

*In-situ* radical (co)polymerization of organic monomers turned out to be quite versatile to achieve higher homogeneity of polystyrene (PSt)/silica gel<sup>25</sup> and poly(*N,N*-dimethylacrylamide) (PDMAAm)/silica gel<sup>26</sup> polymer hybrids (Scheme 10). This *in-situ* polymerization method was further applied to the construction of interpenetrating polymer network (IPN) structure<sup>113</sup> of organic gel and inorganic gel by employing bifunctional organic monomers (crosslinking agents). The resulting IPN polymer hybrids possessed high resistivity to solvent extraction.<sup>28</sup>



**Scheme 10.** Polymer hybrids by *in-situ* polymerization method.

This thesis describes the extension of the organic-inorganic polymer hybrids to possess responsive functions to external stimuli. Combination of the above mentioned chemistry and physics of functional molecules in solid matrices and the novel preparation methods of a wide variety of organic-inorganic polymer hybrids would allow the development of innovative functional materials as well as the better understanding of the nature of the organic-inorganic polymer hybrids.

Polymer hybrids which are responsive to light are reported in Part I. Azobenzene was introduced to poly(2-methyl-2-oxazoline), and the reversible *trans-cis* isomerization behavior in the polymer hybrid was examined. Poly(*N,N*-dimethylacrylamide) having spiropyran chromophore was prepared, and the photochromic behavior in the polymer hybrids was demonstrated. Photo-dimerization of coumarin and thymine groups pending on poly(2-methyl-2-oxazoline) was utilized to the photoresponsive formation of IPN structure in the

polymer hybrids.

Polymer hybrids which are sensitive to heat are presented in Part II. Diels-Alder reaction between maleimide and furan groups was utilized to produce the thermoresponsive IPN polymer hybrids. IPN polymer hybrids of poly(*N*-isopropylacrylamide) gel and silica gel were prepared by *in-situ* polymerization method. The swelling behavior to water and responsiveness to the change of temperature were investigated.

In Part III, solvatochromic pyridinium *N*-phenolate betaine dyes were applied to study the polarity of microenvironment within the polymer hybrids. Investigation on the dispersion of chromophore in the polymer hybrids was carried out.



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## Part I

### Photo-Responsive Organic-Inorganic Polymer Hybrids

## Chapter 1

### Photoresponsive Polymer Hybrids from Azobenzene-Modified Poly(2-methyl-2-oxazoline)s

#### Abstract

Photoresponsive organic-inorganic polymer hybrids were prepared from azobenzene-modified poly(2-methyl-2-oxazoline) (POZO-A) and methyltrimethoxysilane (MeTMOS) or tetramethoxysilane (TMOS). Photo-induced trans-to-cis isomerization and thermal cis-to-trans reverse isomerization were followed by absorption spectroscopy, and the isomerization behavior in polymer hybrids was compared with that in DMSO solution or in film of POZO-A. Two kinds of model compounds were synthesized, and their isomerization behaviors were also examined. The cis isomer ratios in the photostationary state under the irradiation of ultraviolet light were found to be smaller in solid films than in solution. Especially, model compound having triethoxysilyl group showed markedly small cis isomer ratio. Thermal cis-to-trans isomerization was investigated kinetically. Distinct deviation from the first order kinetics was observed in solid films.

## Introduction

Increasing attention has been paid to photochemistry and photophysics of chromophores in amorphous solid matrices such as polymers and sol-gel glasses from both scientific and practical points of view.<sup>1-13</sup> Light-induced change of the structure or the conformation of organic chromophores in glassy solids can be affected by various factors such as polarity and viscosity of the local environment and free volume distribution around the chromophores. Generally the change of the structure or the conformation also induces the change in electronic absorption of the chromophores, and if the absorption changes reversibly in the visible region, it is called photochromic.<sup>14</sup> Investigation of the photochromic behaviors in solid matrices affords valid informations concerning the local environment around the chromophores. Azobenzene chromophores photoisomerize from thermally more stable trans form to less stable cis one by ultraviolet light, and the reverse process takes place both thermally and/or by visible light irradiation.<sup>1-3,15</sup> Kinetic studies of this reversible isomerization have been carried out for azobenzene moieties doped in or covalently incorporated into both organic polymers and sol-gel glasses.<sup>16-26</sup>

Chujo *et al.* have investigated organic-inorganic polymer hybrids, in which organic polymers are dispersed in a silica gel matrix at the molecular level.<sup>27,28</sup> They are prepared by the sol-gel reaction of alkoxysilanes in the presence of organic polymers. As organic-inorganic polymer hybrids are transparent in the visible and near-ultraviolet region, it is of interest to investigate the photochemical/photophysical reaction in the polymer hybrids. This chapter reports an example of photochromic organic-inorganic polymer hybrids by using azobenzene-modified poly(2-methyl-2-oxazoline) as an organic polymer. In the present study, the photoresponsive organic-inorganic polymer hybrids were prepared from azobenzene-modified poly(2-methyl-2-oxazoline) (POZO-A) and tetramethoxysilane (TMOS) or methyltrimethoxysilane (MeTMOS). The present chapter describes the synthesis of the polymer hybrids, the behavior of the trans-to-cis isomerization, and the kinetics of the thermal cis-to-trans isomerization of azobenzene chromophores in the polymer hybrids. They are compared with

those in dilute polymer solution or in polymer film, as well as model compounds doped in sol-gel glass.

## Experimental Section

### Materials

Preparation of poly(2-methyl-2-oxazoline) (POZO) and partial hydrolysis of amide groups of POZO were reported previously.<sup>30</sup> *p*-Phenylazobenzoic acid was prepared by the reaction of *p*-aminobenzoic acid with nitrosobenzene in glacial acetic acid according to a literature.<sup>31</sup> *p*-Phenylazobenzoyl chloride was prepared by the treatment of *p*-phenylazobenzoic acid with thionyl chloride in the presence of anhydrous sodium carbonate according to a literature.<sup>31</sup> Spectroscopic grade DMSO and 0.1 M HCl<sub>aq</sub> were used as received. The following reagents were stored under nitrogen atmosphere. Acetonitrile was dried and distilled from CaH<sub>2</sub>. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was distilled under reduced pressure. Dichloromethane and diethylamine were dried and distilled from CaH<sub>2</sub>. 3-Aminopropyltriethoxysilane was distilled under reduced pressure. Methanol was dried and distilled from magnesium methoxide. Ethanol was dried and distilled from magnesium ethoxide. Tetramethoxysilane (TMOS), methyltrimethoxysilane (MeTMOS), tetraethoxysilane (TEOS), and methyltriethoxysilane (MeTEOS) were distilled. Ethylene glycol was distilled from MgSO<sub>4</sub> under reduced pressure.

### Measurements

<sup>1</sup>H-NMR spectra were recorded on a 270 MHz JEOL-JNM-GX270 NMR spectrometer. <sup>13</sup>C-NMR spectra were recorded on a 67.5 MHz JEOL-JNM-GX270 NMR spectrometer. IR spectra were obtained on a Perkin Elmer 1600 infrared spectrometer. Electronic absorption spectra were obtained on a JASCO V-530 spectrophotometer. Differential scanning calorimetry (DSC) thermograms were recorded with a DSC200, Seiko Instruments Inc., with the heating



rate of 10 °Cmin<sup>-1</sup> under nitrogen atmosphere.

#### Preparation of Azobenzene-Modified Poly(2-methyl-2-oxazoline) (POZO-A)

In a typical procedure, 1.7 mol%-hydrolyzed POZO (4.44 g, 0.89 mmol equivalent NH) was dissolved in acetonitrile (30 ml) under nitrogen atmosphere and DBU (0.20 ml, 1.34 mmol) was added to trap HCl gas. To this solution was added *p*-phenylazobenzoyl chloride (330 mg, 1.35 mmol) and the resulting mixture was stirred overnight at room temperature. The polymer was isolated by reprecipitation from acetonitrile into diethyl ether for two times. Further purification was performed by dialysis with distilled water in order to remove remaining DBU•HCl salt. POZO-A was obtained after freeze-drying with benzene. Yield was 3.76 g (82 %). Degree of modification was calculated from <sup>1</sup>H-NMR and absorption spectra to be 1.2 mol%.

#### Preparation of *N,N*-Diethyl-*p*-phenylazobenzamide (MC-1)

128 mg (0.52 mmol) of *p*-phenylazobenzoyl chloride was dissolved in 10 ml of dry dichloromethane under nitrogen atmosphere. The solution was cooled to 0 °C, and 0.12 ml (1.16 mmol) of diethylamine was added dropwisely. The reaction mixture was stirred for two hours at room temperature. The mixture was poured into water, and the organic layer was washed with water and saturated NaCl<sub>aq</sub>. After evaporation of dichloromethane, crude product was obtained (144 mg). The crude product was applied to a silica column chromatography, using ethyl acetate/hexane (1/2, v/v) as an eluting solvent. The first fraction containing product was concentrated by evaporation and dried under reduced pressure. MC-1 was obtained as an orange viscous liquid. Yield was 139 mg (0.50 mmol, 95 %). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) : δ 1.14 and 1.25 (broad peaks, 6H, CH<sub>3</sub>), 3.29 and 3.57 (broad peaks, 4H, CH<sub>2</sub>), 6.81 - 6.89 (m, 4H, aromatic H of cis isomer), 7.13 - 7.35 (m, 5H, aromatic H of cis isomer), 7.48 - 7.57 (m, 5H, aromatic H of trans isomer), 7.91 - 7.95 (m, 4H, aromatic H of trans isomer). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) : δ 12.76 (br), 14.02 (br), 39.19 (br), 43.07 (br), 122.73, 122.79,

127.04, 128.93, 131.16, 139.34, 152.33, 152.51, 170.26. IR (neat) : 1630 cm<sup>-1</sup> (ν<sub>CO</sub>). Elemental Analysis : Calc. C 72.57, H 6.81, N 14.94 ; Obs. C 72.36, H 6.78, N 14.97. UV/VIS (DMSO) : λ<sub>max</sub><sup>trans</sup> = 328 nm (ε = 2.38 × 10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>), 447 nm (ε = 670 M<sup>-1</sup>cm<sup>-1</sup>). λ<sub>max</sub><sup>cis</sup> = 435 nm (ε = 1.37 × 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>).

#### Preparation of *N*-3-Triethoxysilylpropyl-*p*-phenylazobenzamide (MC-2)

126 mg (0.51 mmol) of *p*-phenylazobenzoyl chloride was dissolved in 10 ml of dry dichloromethane under nitrogen. The solution was cooled to 0 °C and then 0.25 ml (1.07 mmol) of 3-aminopropyltriethoxysilane was added. The reaction mixture was stirred for two hours at room temperature. After evaporation of the solvent, crude product was applied to a silica column chromatography, using ethyl acetate/hexane (1/2, v/v) as an eluting solvent. The first fraction containing product was concentrated by evaporation and dried under reduced pressure. MC-2 was obtained as an orange solid. Yield was 180.5 mg (0.42 mmol, 82 %). Mp. 107 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) : δ 0.74 (t, 2H, J = 7.76 Hz, CH<sub>2</sub>Si), 1.23 (t, J = 6.93 Hz, 9H, CH<sub>3</sub>), 1.80 (m, 2H, C-CH<sub>2</sub>-C), 3.51 (m, 2H, CH<sub>2</sub>N), 3.84 (q, J = 6.93 Hz, 6H, SiO-CH<sub>2</sub>), 6.64 (broad s, 1H, NH), 7.50 - 7.56 (m, 3H, aromatic), 7.91 - 7.98 (m, 6H, aromatic). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) : δ 7.84, 18.22, 22.79, 42.27, 58.47, 122.77, 122.98, 127.84, 129.08, 131.43, 136.68, 152.49, 154.03, 166.70. IR (neat) : 3300 (ν<sub>NH</sub>), 1632 (ν<sub>CO</sub>), 1545 (δ<sub>NH</sub>), 1079 (ν<sub>SiO</sub>). Elemental Analysis : Calc. C 61.51, H 7.27, N 9.78 ; Obs. C 61.25, H 7.34, N 9.80.

#### Preparation of Organic-Inorganic Polymer Hybrids from POZO-A

A typical procedure is as follows. POZO-A and alkoxysilane were dissolved into methanol (10 times in volume to alkoxysilane). A drop of aqueous HCl (0.1 M) was added to the solution and the mixture was stirred for 30 minutes. Then the mixture was placed in a polypropylene mold covered with thin paper towel, and left in air at room temperature. After a few days solvents were removed by evaporation and POZO-A/silica gel polymer hybrid was obtained as a glassy material.

*Preparation of Film Samples for Isomerization Study*

Samples for isomerization study were prepared by casting the reaction mixture on quartz substrates (10 mm × 45 mm). The surface of the substrates has to be very clean to obtain good homogeneous wetting. The plates were immersed for 24 hours in a neutral detergent solution and then ultrasonically agitated in concentrated HNO<sub>3</sub> for 10 minutes, washed well with distilled water and then methanol, dried and kept in a desiccator. In cases of the polymer hybrids using TMOS, ethylene glycol (quarter volume to alcohol solvent) was added to the reaction mixture before casting to avoid cracking. The films were kept at room temperature for 24 hours and then heated at 120 °C for 12 hours to complete the sol-gel reaction. Sol-gel films with model compounds were prepared in the same way. Concentration of the chromophore was set to be comparable to that of the polymer hybrid film. Thickness of the films was ca. 100 μm.

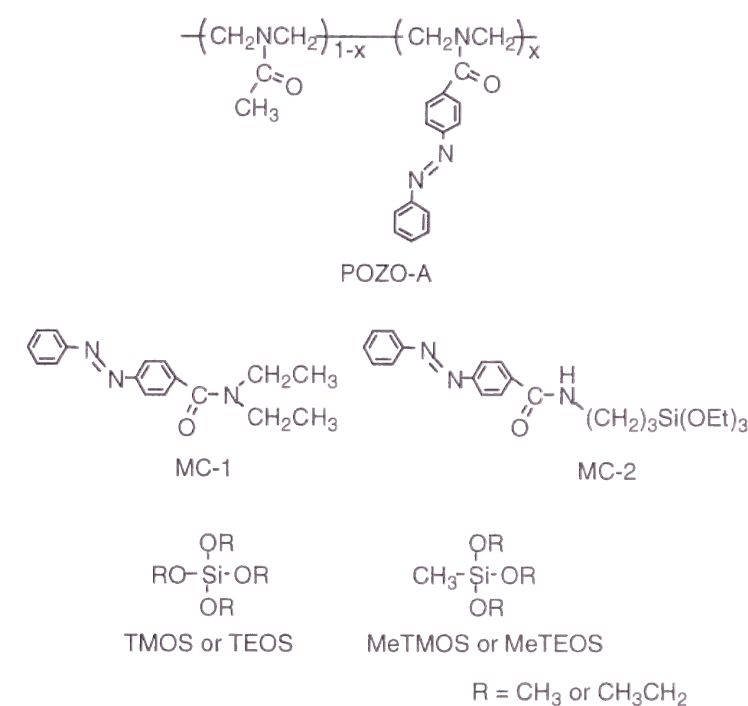
POZO-A film was also prepared on a quartz substrate by casting a methanol solution of POZO-A. It was kept at room temperature for 24 hours and then heated at 70 °C in vacuo for 7 hours to remove residual solvent.

*Measurements of Photoisomerization and Thermal Isomerization Processes*

A sample was irradiated with ultraviolet light at room temperature to induce the trans-to-cis photoisomerization of azobenzene chromophores. As a ultraviolet light source, 450 W high-pressure mercury lamp (Ushio UM-452) was used with a Pyrex cooler and a glass filter (Toshiba UV-D33S) to cut off the wavelengths below 300 nm and visible region. The reaction was followed by absorption spectra. To follow the cis-to-trans reverse isomerization process, the sample was equilibrated with ultraviolet light beforehand. Then it was placed in a temperature controlled box for thermal cis-to-trans reverse isomerization process. The reaction was also followed by absorption spectra.

**Results and Discussion***Preparation of POZO-A*

Poly(2-methyl-2-oxazoline) (POZO) was prepared by the ring-opening polymerization of 2-methyl-2-oxazoline initiated by methyl tosylate. POZO was refluxed with aqueous NaOH solution to give partially hydrolyzed POZO (H-POZO). Degree of hydrolysis could be controlled by the molar ratio of the amide groups to NaOH. Poly(2-methyl-2-oxazoline)s with various azobenzene contents (POZO-A) were prepared by the reaction of H-POZO with *p*-phenylazobenzoyl chloride in acetonitrile. Triethylamine or DBU was used to trap generated HCl. The results of the preparation of POZO-A are summarized in Table 1. It is confirmed that almost quantitative introduction of azobenzene moieties as pendant groups into POZO could be achieved by this method. Two types of model compounds (MC-1 and MC-2 in Figure 1) were synthesized by the condensation reaction of *p*-phenylazobenzoyl chloride with diethylamine and 3-aminopropyltriethoxysilane, respectively, and used as a model compound for the isomerization reaction of azobenzene moieties.



**Figure 1.** Chemical structures of POZO-A, model compounds, and alkoxy silanes.



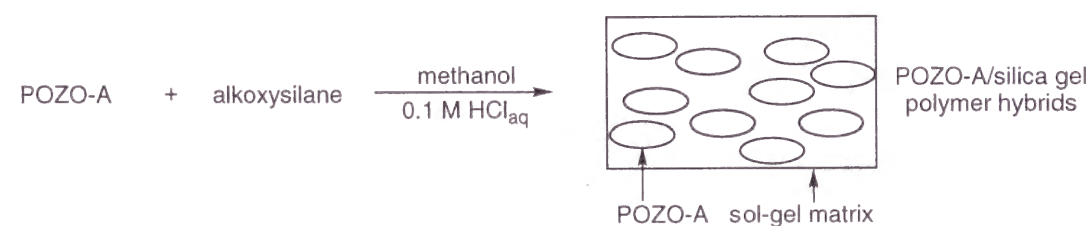
**Table 1.** Preparation of azobenzene-modified poly(2-methyl-2-oxazoline) (POZO-A)

Run	POZO	H-POZO	Yield(%)	POZO-A	
	Degree of Polymerization <sup>a</sup>	Degree of Hydrolysis <sup>a</sup>		Degree of Modification UV <sup>b</sup>	<sup>1</sup> H-NMR <sup>c</sup>
1	32	2.8	95	2.0	2.0
2	74	1.3	85	1.3	1.3
3	~100	1.7	85	1.2	1.2
4	32	19.2	~100	9.4	16.0
5	45	9.6	98	6.3	9.4

<sup>a</sup> Determined from <sup>1</sup>H-NMR spectra. <sup>b</sup> Calculated from UV spectra at  $\lambda_{\text{max}} = 328 \text{ nm}$  ( $\epsilon_{\text{max}} = 2.38 \times 10^4$ ).<sup>c</sup> Calculated from <sup>1</sup>H-NMR spectra (acetyl protons v.s. ring protons).

### POZO-A/Silica Polymer Hybrids

The organic-inorganic polymer hybrids were prepared from POZO-A by utilizing the sol-gel reaction of various kinds of alkoxysilanes (Scheme 1). POZO-A and alkoxysilanes were dissolved into methanol, and aqueous HCl was added as a catalyst for the sol-gel reaction. The mixture was stirred for a certain period in a sealed bottle and then placed in an open container covered with a paper towel under air atmosphere at room temperature. The results are summarized in Table 2. Transparent and homogeneous polymer hybrids were obtained when methyltrimethoxysilane (MeTMOS) and tetramethoxysilane (TMOS) were used as the alkoxysilanes. The feed ratio of the polymer to silicate (w/w) could be varied between 1/5 and 2 without any influence in the homogeneity (runs 5~8). Differences of molecular weight and the content of azobenzene moieties up to 16 mol% also seem to have little effect on the homogeneity of polymer hybrids.

**Scheme 1****Table 2.** Preparation of POZO-A / alkoxysilane polymer hybrids<sup>a</sup>

run	POZO-A <sup>b</sup>	alkoxysilane	ratio <sup>c</sup>	appearance
1	1(2.0)	MeTMOS	1 / 5	transparent, homogeneous no cracks
2	2(1.3)	MeTMOS	1 / 5	transparent, homogeneous no cracks
3	3(1.2)	MeTMOS	1 / 5	transparent, homogeneous no cracks
4	4(16.0)	MeTMOS	1 / 5	transparent, homogeneous no cracks
5	5(9.4)	MeTMOS	1 / 5	transparent, homogeneous no cracks
6	5(9.4)	MeTMOS	1 / 2	transparent, homogeneous no cracks
7	5(9.4)	MeTMOS	1 / 1	transparent, homogeneous no cracks
8	5(9.4)	MeTMOS	2 / 1	transparent, homogeneous no cracks
9	3(1.2)	TMOS	1 / 5	transparent, homogeneous cracks
10	3(1.2)	EtTMOS	1 / 5	turbid
11	3(1.2)	<i>i</i> -BuTMOS	1 / 5	turbid
12	3(1.2)	PhTMOS	1 / 5	turbid, phase separated

<sup>a</sup> Methanol was used as a solvent and a drop of 0.1 M HCl<sub>aq</sub> was added as a catalyst for the sol-gel reaction. <sup>b</sup> Degree of modification is shown in parentheses. (calculated from <sup>1</sup>H-NMR spectra). <sup>c</sup> POZO-A / alkoxysilane (w/w).

According to the previous studies, it is known that stretching bands of amide carbonyl groups ( $\nu_{\text{C=O}}$ ) are shifted to lower wavenumbers region in polymer hybrid due to the hydrogen-bond formation between carbonyl groups and residual silanol groups. In POZO-A/MeTMOS polymer hybrid,  $\nu_{\text{C=O}}$  shifted to lower wavenumbers region about  $8 \text{ cm}^{-1}$  compared with that of POZO-A. This result indicates that the hydrogen-bond is formed in the same manner in POZO-A/MeTMOS system, which is considered to be responsible for the molecular level homogeneity. In the cases of using MeTMOS, the obtained polymer hybrids had no cracks after the complete removal of the solvent and flexible to some extent after completion of the condensation reaction of alkoxysilane, whereas in the case of TMOS, only cracked polymer hybrids were obtained. Therefore POZO-A/MeTMOS was used for further investigation as the film can be formed easily on quartz substrate. On the other hand, ethyltrimethoxysilane (EtTMOS), isobutyltrimethoxysilane (*i*-BuTMOS) and phenyltrimethoxysilane (PhTMOS) gave only heterogeneous polymer hybrids under the same condition.

Glass transition temperature,  $T_g$ , which is defined as the midpoint of the glass transition in DSC thermograms, of POZO-A was observed at 78 °C.  $T_g$  of POZO-A/MeTMOS (1/10) polymer hybrid was found at 82 °C, indicating that the segment mobility of organic polymer in the polymer hybrids from tri-functional alkoxysilane (MeTMOS) is comparable to that of polymer itself. On the contrary, no well-defined glass transition was observed for POZO-A/TMOS (1/10) polymer hybrid. This result suggests a good dispersion of the organic polymer chains in the silica gel network.<sup>32,33</sup>

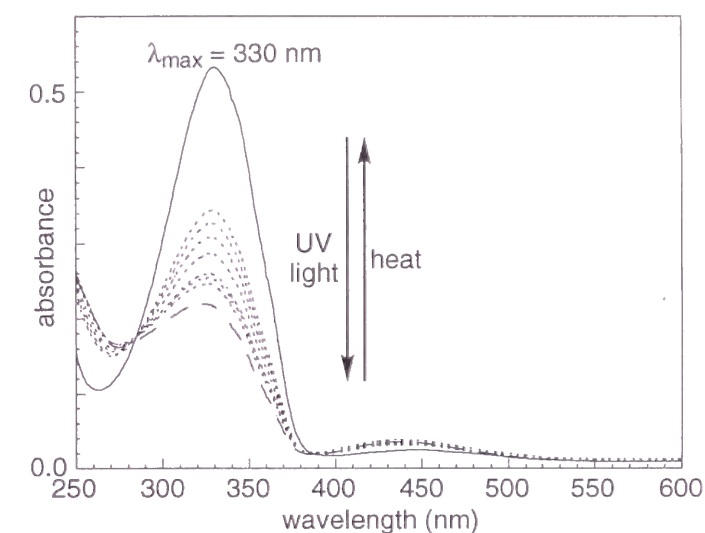
#### Photochemical Trans-to-Cis Isomerization

To examine the isomerization behavior of azobenzene chromophores in the polymer hybrids, photochemical trans-to-cis isomerization and thermal cis-to-trans reverse isomerization were investigated and compared with a solution or a film of POZO-A as well as model compounds in sol-gel glasses. All samples studied are listed in Table 3 with absorption maximum wavelengths ( $\lambda_{\max}$ ). It was found that the shape of absorption and  $\lambda_{\max}$  of all the samples were almost the same. Therefore it can be concluded that the difference of the electronic interaction between the azobenzene chromophores and the surroundings can be ignored.

**Table 3.** Absorption maximum wavelength and cis fraction in the photostationary state for all samples.

	$\lambda_{\max}$ (nm)	%cis
MC-1 (in DMSO)	328	90
POZO-A <sup>a</sup> (in DMSO)	330	85
POZO-A <sup>a</sup> (film)	330	63
POZO-A/MeTMOS <sup>a,b</sup> (film)	330	63
POZO-A/TMOS <sup>a,b</sup> (film)	329	58
MC-2/MeTEOS (film)	323	54
MC-2/POZO/TEOS (film)	327	50

<sup>a</sup>POZO-A :  $M_n = 8,500$ , degree of modification = 1.2 mol% (calculated from <sup>1</sup>H NMR spectrum). <sup>b</sup>POZO-A/alkoxysilane = 1/10 (w/w).



**Figure 2.** Absorbance spectra of POZO-A/MeTMOS polymer hybrid film. Solid line : thermal equilibrium; broken line : photostationary state under UV irradiation; dotted lines : thermal recovery of absorbance at 60 °C (every 30 min).

The photoisomerization of azobenzene chromophores from trans form to cis one was induced by the irradiation of ultraviolet light with wavelengths between 300 and 400 nm from a high-pressure mercury lamp through a Pyrex cooler and a glass filter. Photostationary state was achieved within 20 min in all the samples. As a typical example, absorption spectra of POZO-A/MeTMOS polymer hybrid film in thermal equilibrium (solid line) and in photostationary state (broken line) are shown in Figure 2. The fraction of cis isomer was calculated from the absorbance ( $A$ ) at  $\lambda_{\max}$  for the  $\pi$ - $\pi^*$  absorption of the trans isomer at time  $t$  according to the equation<sup>23</sup>

$$[\text{cis}]_t/[\text{trans}]_0 = (1 - A/A_0)/(1 - \epsilon_{\text{cis}}/\epsilon_{\text{trans}}) \quad (\text{eq. 1})$$

where  $[\text{cis}]_t$  is the concentration of the cis isomer at time  $t$ ,  $[\text{trans}]_0$  is the initial concentration of the trans isomer,  $A_0$  is the initial absorbance at  $\lambda_{\max}$ , and  $\epsilon_{\text{cis}}/\epsilon_{\text{trans}}$  is the ratio of the molar



absorption coefficients of the cis and trans isomers at  $\lambda_{\max}$ . The  $\epsilon_{\text{cis}}/\epsilon_{\text{trans}}$  value in the present study was determined from the absorption spectra and  $^1\text{H-NMR}$  spectra of MC-1 in DMSO solution in the initial state and in the photostationary state. Before the irradiation of ultraviolet light, the peaks for aromatic protons which correspond to trans isomers were observed between 7.8 and 8.3 ppm. After the irradiation of ultraviolet light, the peaks for trans isomers decreased and new peaks corresponding to cis form appeared between 7.1 and 7.7 ppm. From the integral of these protons, the ratio of trans and cis isomers in the photostationary state could be calculated to be 10 to 90. From this result and the absorption spectra of MC-1 in DMSO, the  $\epsilon_{\text{cis}}/\epsilon_{\text{trans}}$  value was estimated to be  $3.78 \times 10^{-2}$ .

Cis fractions in the photostationary state calculated for other samples are also summarized in Table 3. Firstly, it is noticed that the cis fractions of film samples turned out to be smaller than those in solution, indicating the inhibition of the photoisomerization due to a relatively small free volume in the solid matrices compared with that in solution. The same phenomena were found in other systems.<sup>26</sup> Moreover, the photoisomerization was hindered rather more strongly in the samples using TMOS and TEOS than those with MeTMOS and MeTEOS. This might reflect the rigidity of the silica matrices. Tetra-functional alkoxysilanes generate more rigid silica matrices than tri-functional ones. Movement of the azobenzene chromophores directly attached to the silica matrices (MC-2) seems to be more restricted than those in the polymer hybrids, even in the presence of the additional organic polymer. This might suggest that the introduction of the chromophore on the polymer chain brought about some differences of the local environment for the chromophores in the polymer hybrids.

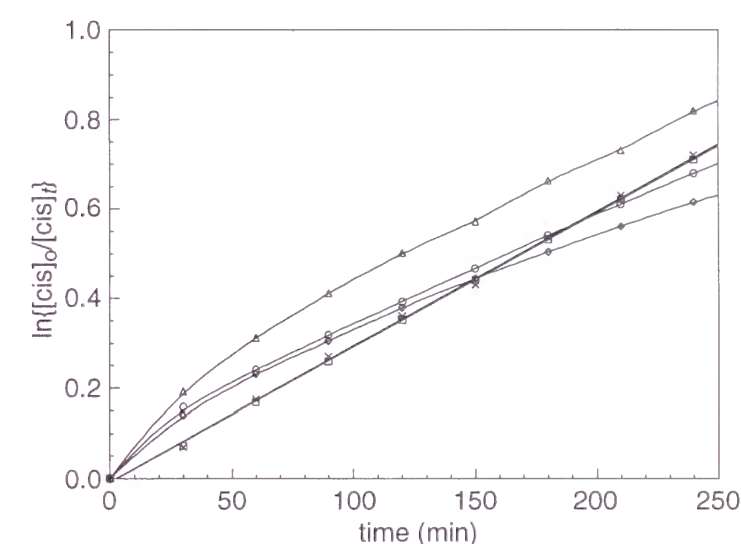
#### Kinetics of Thermal Cis-to-Trans Reverse Isomerization

Thermodynamically unstable cis isomer isomerizes thermally to the more stable trans form. Dotted lines in Figure 2 are the changes of absorption during the thermal cis-to-trans isomerization at 60°C (every 30 min). Absorbance of the  $\pi-\pi^*$  band of trans isomer around 330 nm increased progressively with time and finally the initial absorbance was recovered.

The kinetics of the thermal cis-to-trans isomerization were analyzed according to the equation

$$\ln\{[\text{cis}]_0/[\text{cis}]_t\} = kt \quad (\text{eq. 2})$$

where  $[\text{cis}]_0$  and  $[\text{cis}]_t$  were the concentration of the cis isomer in the photostationary state (time  $t = 0$ ) and at time  $t$  (min), respectively, which were calculated from equation 1, and  $k$  is the first-order rate constant for the thermal cis-to-trans isomerization.



**Figure 3.** First-order plots for the thermal cis-to-trans isomerization at 60 °C: square, MC-1 in DMSO; cross, POZO-A in DMSO; diamond, POZO-A film; circle, POZO-A/MeTMOS polymer hybrid; triangle, POZO-A/TMOS polymer hybrid.

**Table 2.** Fraction of the fast process ( $\alpha$ ) and kinetic parameters of thermal cis-to-trans isomerization.

	60 °C			85 °C		
	$\alpha$	$k_{\text{fast}}$ ( $10^{-2}\text{min}^{-1}$ )	$k_{\text{slow}}$ ( $10^{-3}\text{min}^{-1}$ )	$\alpha$	$k_{\text{fast}}$ ( $10^{-1}\text{min}^{-1}$ )	$k_{\text{slow}}$ ( $10^{-2}\text{min}^{-1}$ )
MC-1 (DMSO)	0	-	2.9	-	-	-
POZO-A	0.15	2.5	1.9	0.14	2.1	2.6
POZO-A/MeTMOS (1/10)	0.12	6.2	2.6	0.11	2.1	2.6
POZO-A/TMOS (1/10)	0.17	3.4	2.6	0.11	2.0	2.8



The first-order plots for the thermal cis-to-trans isomerization at 60 °C in the polymer hybrids are shown in Figure 3 with those of POZO-A and MC-1 in DMSO solution and in POZO-A film. The isomerization in solution was found to follow first-order kinetics, and the rates were almost the same between MC-1 and POZO-A. On the other hand, deviation from first-order kinetics was observed in solid film samples. In the early stage of the reaction the isomerization in films proceeded faster than in solutions. It gradually decelerated and finally the rates became the slower values than those in solutions. The existence of such anomalously fast components for thermal reverse isomerization has been found often in solid matrices,<sup>16,18b,18c,19c,20b,21c,22,23</sup> and attributed to the trapping of some of cis isomer in a strained conformation during UV irradiation. Such strained-cis species can return more easily to the trans form than the relaxed-cis species. Non-monoexponential decay kinetics of unimolecular reactions in amorphous polymers have been described by many kinetic models.<sup>6</sup> One of the simplest model introduces a sum of two or more exponential terms to fit the decay kinetics.<sup>34</sup> Biexponential equation 3,<sup>25</sup>

$$[\text{cis}]/[\text{cis}]_0 = \alpha \exp(-k_{\text{fast}}t) + (1-\alpha) \exp(-k_{\text{slow}}t) \quad (\text{eq. 3})$$

where  $\alpha$  is the fraction of the fast species and  $k_{\text{fast}}$  and  $k_{\text{slow}}$  are the rate constants for the fast and slow processes, respectively, fitted the experimental data quite well. Table 4 summarizes the fitting parameters. The relative rate constant for the fast process ( $k_{\text{fast}}$ ) appears to differ from  $k_{\text{slow}}$  by one order of magnitude, and the fraction of the fast process ( $\alpha$ ) was about 15%. These values are comparable with the previous studies.<sup>20b,22a</sup> The same analysis was carried out for the thermal cis-to-trans isomerization at 85 °C (Table 4). At both temperatures, difference of the kinetic parameters among POZO-A, POZO-A/MeTMOS, and POZO-A/TMOS was not so large. Recently we have found that a solvatochromic chromophore in the polymer hybrids was relatively insensitive to the polarity of silica matrices,<sup>35</sup> which might be due to the presence of organic polymer between the chromophore and the silica matrices. The result

of the kinetic study of the cis-to-trans isomerization of azobenzene chromophore in the polymer hybrids seems to indicate the same situation.

## Conclusion

Azobenzene chromophore was introduced on the side chain of poly(2-methyl-2-oxazoline) (POZO-A) and organic-inorganic polymer hybrids were prepared from POZO-A. Transparent and homogeneous polymer hybrids were obtained in a wide range of polymer to silicate. Photoinduced trans-to-cis and thermal cis-to-trans isomerization of azobenzene chromophore in the polymer hybrids were investigated. Kinetic study of the cis-to-trans isomerization revealed that the mobility of the chromophore in the polymer hybrid was comparable to that in polymer itself. The local environment surrounding the chromophore might possess the characteristics of organic polymer. Further studies on thermal cis-to-trans isomerization for polymer hybrids with different polymer/silicate ratio as well as MC-2/silica samples are required to clarify the effect of organic polymer for the isomerization behavior of azobenzene in the polymer hybrids.

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## Chapter 2

**Photochromic Polymer Hybrids from Spiropyran-Modified  
Poly(*N,N*-dimethylacrylamide)**

## Abstract

Photochromic organic-inorganic polymer hybrids were prepared by the sol-gel reaction of tetramethoxysilane (TMOS) in the presence of spiropyran-modified poly(*N,N*-dimethylacrylamide) **3**. The obtained polymer hybrids were characterized by thermogravimetric analysis (TGA) and FT-IR, and photochromic behavior was followed by electronic absorption spectroscopy. Upon an irradiation of ultraviolet light, an absorption around 557 nm appeared in the visible region and the color of the hybrid turned to be violet. The effect of silica gel on the isomerization behavior seemed to be relatively small.



## Introduction

Preparation of molecular composites of organic materials and inorganic ones has attracted much attentions in the field of materials science.<sup>1-5</sup> Sol-gel technique of alkoxysilanes is widely employed to form silica gel at low temperature in the presence of organic compounds.<sup>6</sup> The sol-gel reaction comprises the hydrolysis of Si-OR groups to Si-OH (silanol) groups and the condensation of the silanol groups into -Si-O-Si- linkages. Three-dimensional silica gel is constructed as a result.

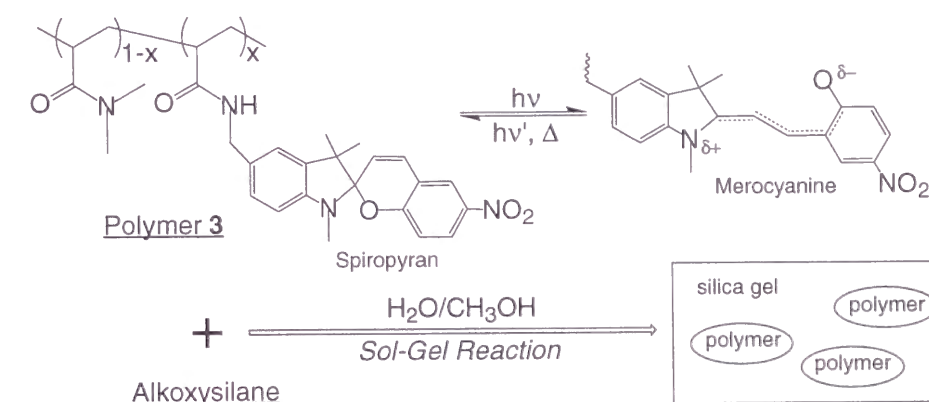
Chujo *et al.* have investigated organic-inorganic polymer hybrids, where organic polymers were dispersed at the molecular level in a silica gel matrix.<sup>1,7</sup> They are prepared by the sol-gel reaction of alkoxysilanes in the presence of organic polymers such as poly(2-methyl-2-oxazoline), poly(*N*-vinylpyrrolidone), and poly(*N,N*-dimethylacrylamide). It was found that the hydrogen bonding interactions between the silanol groups on the silica gel and the amide groups of the organic polymers play a critical role to achieve the molecular-level homogeneity.

On the other hand, photochromic materials have been investigated intensively so far from both scientific and applicational viewpoints.<sup>8-13</sup> Spiropyran is one of the most well-known photochromic chromophore that photoisomerizes from spiropyran form to merocyanine structure by the irradiation of ultraviolet light.<sup>14</sup> The reverse reaction proceeds thermally or by visible light irradiation. The merocyanine is colored while the spiropyran is colorless. The photochromic band of merocyanine in the visible region is known to be solvatochromic, that is, the absorption shifts depending on the polarity of the solvent and the color changes.

Isomerization behavior of spiropyran in sol-gel matrices has been found to be somewhat complicated compared with that in solutions or in organic polymer films.<sup>15-19</sup> The formation of the strong hydrogen bondings between O<sup>δ-</sup> of merocyanine and the silanol groups of silica gels stabilizes the colored merocyanine form, and the reverse photochromism has been observed. It is of interest to investigate the isomerization behavior of spiropyran in the organic-inorganic polymer hybrids since they possess a unique morphology composed of organic polymer and

silica gel. Little has been known about the microenvironment surrounding the dye in the polymer hybrids. As mentioned above, the absorption of the photochromic band of the chromophore is solvatochromic. Microscopic information around the chromophore can be estimated from this phenomena.

This chapter demonstrates the synthesis and characterization of photochromic polymer hybrids from spiropyran-modified poly(*N,N*-dimethylacrylamide) **3** (Scheme 1).



**Scheme 1.** Preparation of Photochromic Polymer Hybrids via Sol-Gel Reaction.

## Experimental Section

### Materials

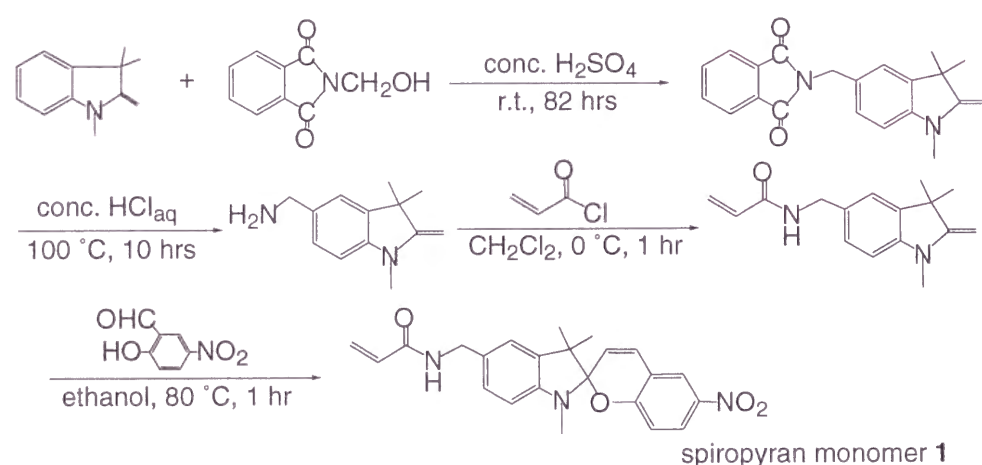
1,3,3-Trimethyl-2-methyleneindoline was distilled under reduced pressure. *N*-Hydroxymethylphthalimide and 5-nitrosalicylaldehyde were used as received. Acryloyl chloride and *N,N*-dimethylacrylamide were distilled under reduced pressure and stored under nitrogen atmosphere in a refrigerator. Dichloromethane, chloroform, and triethylamine were dried and distilled from CaH<sub>2</sub>. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol below 30 °C. Tetramethoxysilane (TMOS) was distilled and stored under nitrogen atmosphere. Methanol was dried and distilled from magnesium methoxide and stored under nitrogen atmosphere.

### General

<sup>1</sup>H-NMR spectra were recorded on a 270 MHz JEOL-JNM-GX270 NMR spectrometer. IR spectra were obtained on a Perkin Elmer 1600 infrared spectrometer. Electronic absorption spectra were obtained on a JASCO V-530 spectrophotometer. Differential scanning calorimetry (DSC) thermograms were recorded with a DSC200, SEIKO Instruments Inc., with a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. Thermogravimetric analyses (TGA) were carried out on a TG/DTA6200, SEIKO Instruments, Inc., with a heating rate of 10 °C min<sup>-1</sup> under air. Gel permeation chromatographic analysis (GPC) was conducted with a Tosoh TSKgel α-3000 column by using DMSO + LiCl (10mM) as an eluent at 50 °C after calibration with standard poly(oxyethylene).

### Monomer Synthesis

Spiropyran monomer **1** was synthesized by following the route depicted in Scheme 2 according to a procedure described by Labsky *et al.*<sup>20</sup>



**Scheme 2.** Route to the synthesis of spiropyran monomer **1**.

### Polymer Synthesis

Copolymer of *N,N*-dimethylacrylamide (**2**) and spiropyran monomer **1** was prepared

by radical copolymerization initiated by AIBN. 2.4 g of **2** (24 mmol), 0.10 g of **1** (0.25 mmol), and 0.20 g of AIBN (1.2 mmol) were dissolved in 20 ml of chloroform under nitrogen atmosphere. The solution was heated at 60 °C for 24 h, and polymer was isolated by reprecipitation into hexane. The resulting polymer **3** was further purified by reprecipitation from chloroform into hexane for two times, and freeze-dried with benzene. Yield was 2.5 g. The structure was confirmed from <sup>1</sup>H-NMR, IR, and absorption spectra. The molecular weight was estimated by GPC to be  $M_w = 32,500$ ,  $M_n = 8,600$ ,  $M_w/M_n = 3.79$ . The spiropyran content was calculated from the absorption spectrum to be 1.1 mol%, which corresponded well with the feed ratio of **1** and **2**.

### Preparation of Polymer Hybrids from Polymer (**3**)

Polymer **3** and TMOS were dissolved in methanol and water (4 equivalents to TMOS) was added. The resulting mixture was stirred at room temperature for 1 h in a sealed bottle. Then the mixture was placed in a polypropylene mold covered with a paper towel and left in air at room temperature. After removal of the solvent by evaporation, polymer hybrids were obtained as glassy solids. Polymer hybrid films for absorption measurement were prepared by casting the reaction mixture onto glass slides.

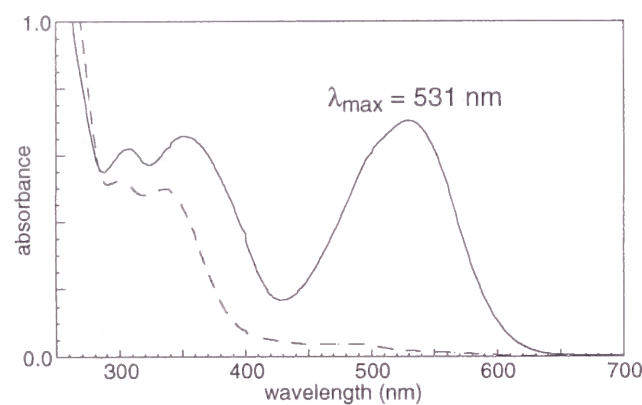
### Measurements of Photochromism

A sample was irradiated with ultraviolet light at room temperature to induce the photoisomerization of spiropyran chromophores. 300W Xe lamp filtered with a Toshiba UV-D33S glass filter was employed as a source of ultraviolet light. The reaction was followed by absorption spectra.



## Results and discussion

Spiropyran-modified poly(*N,N*-dimethylacrylamide) **3** was successfully synthesized by the radical copolymerization of *N,N*-dimethylacrylamide and spiropyran monomer **2**. Figure 1 shows the absorption spectra of polymer **3** in methanol before and after the irradiation of ultraviolet light. A new absorption band appeared after irradiation, indicating that the spiropyran chromophore was actually incorporated into polymer. This band showed solvatochromism, namely, the absorption maximum wavelength was 489 nm in water, 531 nm in methanol, and 566 nm in DMF. As the merocyanine form of the chromophore possesses high intrinsic polarity, the visible absorption maximum shifts shorter wavelengths in more polar solvents.



**Figure 1.** Absorption spectra of polymer **3** in methanol before (broken line) and after (solid line) UV irradiation.

Photochromic polymer hybrids were then prepared via the sol-gel reaction of TMOS in the presence of polymer **3**. Acid catalyst was not employed for the sol-gel reaction since protonation on nitrogen atom of indoline ring of the chromophore changes the photochromic behavior. Thus polymer **3** and TMOS were dissolved in methanol, water of 4 equivalents to TMOS was added, stirred for 1 h in a sealed bottle to make the sol-gel reaction of TMOS proceed to some degree, and the resulting mixture was left in air to dryness. The results of the preparation of polymer hybrids are summarized in Table 1. The obtained polymer hybrids were optically transparent and homogeneous in all the examined weight ratios of polymer **3**

**Table 1.** Polymer Hybrids from Polymer **3** and TMOS.<sup>a</sup>

run	polymer <b>3</b> (mg)	TMOS (mg)	appearance	polymer content (wt%)		T <sub>10</sub> <sup>c</sup> (°C)	ν <sub>co</sub> <sup>d</sup> (cm <sup>-1</sup> )
				calcd.	obsd. <sup>b</sup>		
1	200	250	transparent	66.9	72.1	335	1629
2	200	500	transparent	50.3	64.0	360	1632
3	200	1,000	transparent	33.6	43.6	372	1631
polymer <b>3</b>						356	1639

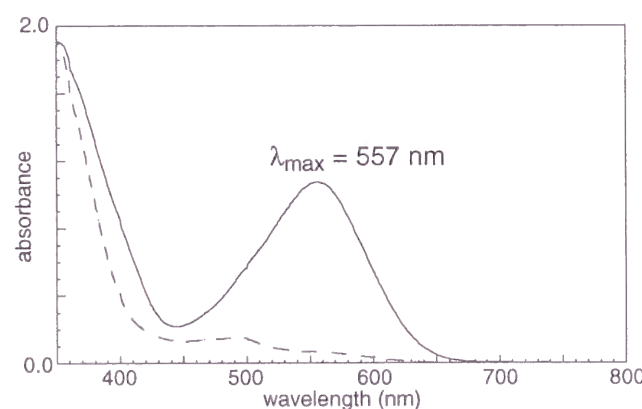
<sup>a</sup> 2 ml of methanol was used as a solvent. 4 equivalents of water (to TMOS) was added to the mixture.

<sup>b</sup> Total weight loss by heating up to 1000 °C in air, observed by TGA. <sup>c</sup> 10 wt% weight loss temperature observed by TGA. <sup>d</sup> Wavenumbers of amide carbonyl stretching band observed by FT-IR.

to TMOS. Polymer contents observed by TGA were found to be somewhat larger than expected. Sol-gel reaction of TMOS without acid catalyst might be incomplete, though the weight ratio of polymer to silica gel could be varied widely. And the polymer hybrids with higher silica weight ratio showed higher thermal stability. The hydrogen bonding interactions between polymer and silica gel were confirmed by FT-IR. The stretching band of amide carbonyl group shifts to lower wavenumber region by hydrogen bonding interaction with silanol groups on silica gel. Polymer **3** has its original carbonyl peak at 1639 cm<sup>-1</sup> and it shifts to about 1630 cm<sup>-1</sup> by the formation of hydrogen bonding in the polymer hybrids. In the previous study, the degree of the shift of carbonyl vibration for poly(*N,N*-dimethylacrylamide)/TMOS polymer hybrids was found to be 18 cm<sup>-1</sup>.<sup>1</sup> In the present system, the hydrogen bonding interactions between polymer and silica gel seem to be weaker though the main chain structure is same. It might be the result from the fact that acid catalyst was not employed in this study.

Photochromic behavior of chromophore in the polymer hybrids was then examined. When spiropyran chromophore is doped in or adsorbed on silica gel, the color turns red.<sup>15-19</sup> It can be attributed to the open merocyanine form of the chromophore. Moreover, this red color is thermally stable and disappears upon the irradiation of ultraviolet light. This reverse photochromism is considered to be the result from the formation of strong hydrogen bondings

between merocyanine chromophores and silanols. All the polymer hybrids prepared were, however, found to be colorless. And the color turned violet upon the irradiation of the ultraviolet light. Absorption spectra of polymer hybrid before and after the irradiation of ultraviolet light are shown in Figure 2. The absorption maximum wavelengths were found to be 557 nm for the polymer hybrids (runs 1-3), and that for the polymer **3** itself in the film state was 559 nm. The color faded slowly when the sample was kept in the dark at room temperature, and the coloration-decoloration processes could be repeated. Therefore spiropyran chromophores in the polymer hybrids isomerize normally in spite of the presence of silica gels. From these results, the spiropyran chromophores in the polymer hybrids seem to be surrounded by organic polymer preferably, and the effect of silica gel on the photochromic behavior of the chromophore is relatively small. In our previous report, the solvatochromic chromophore was found to undergo the polymer-rich environment in the polymer hybrids where the domain size of the organic polymer was  $< 4$  nm.<sup>21</sup> In the current system, the same phenomena seem to occur. Further investigation on the isomerization actions, especially kinetics, will allow us better understandings on the correlation between the microenvironment around the chromophore and the photochromic behavior.



**Figure 2.** Absorption spectra of polymer hybrid (run 2) before (broken line) and after (solid line) UV irradiation.

## Conclusion

Poly(*N,N*-dimethylacrylamide) having spiropyran chromophores on the side chain (**3**) was synthesized by the radical copolymerization of *N,N*-dimethylacrylamide and spiropyran monomer **2**. Polymer **3** showed photochromic behavior upon the irradiation of the ultraviolet light. Photochromic organic-inorganic polymer hybrids were prepared by utilizing the sol-gel reaction of TMOS in the presence of polymer **3**. No acid catalyst was employed to avoid the protonation on the spiropyran chromophore. Transparent and homogeneous polymer hybrids could be obtained in all the weight ratios of polymer to silicate. The resulting polymer hybrids were characterized by TGA, FT-IR, and absorption spectra. Spiropyran chromophores in the polymer hybrids photoisomerize normally in spite of the existence of the silica gel. This might indicate the preferable solvation of the chromophore by organic polymer than by silica gel.

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## Chapter 3

### Photochemically Reversible IPN Polymer Hybrids Utilizing the Photodimerization of Coumarin

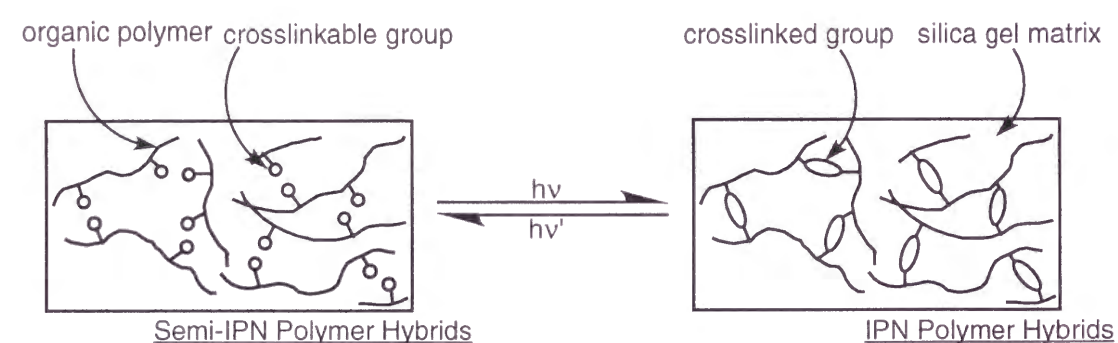
#### Abstract

A new strategy to prepare organic-inorganic polymer hybrids having interpenetrating polymer network (IPN) structure is presented. Polymer hybrids were synthesized from poly(2-methyl-2-oxazoline) having coumarin moieties as reversibly photo-crosslinkable side groups (**4**). It was found that the concentration of acid catalyst for sol-gel reaction of tetramethoxysilane (TMOS) was essential to obtain transparent and homogeneous polymer hybrids. Reversible photo-dimerization of coumarin groups took place in the polymer hybrids by the irradiation of light with different wavelengths. The resulting polymer hybrids are IPN of organic gel and silica gel. Solvent-resistant property of the polymer hybrids was improved by formation of the IPN structure.



## Introduction

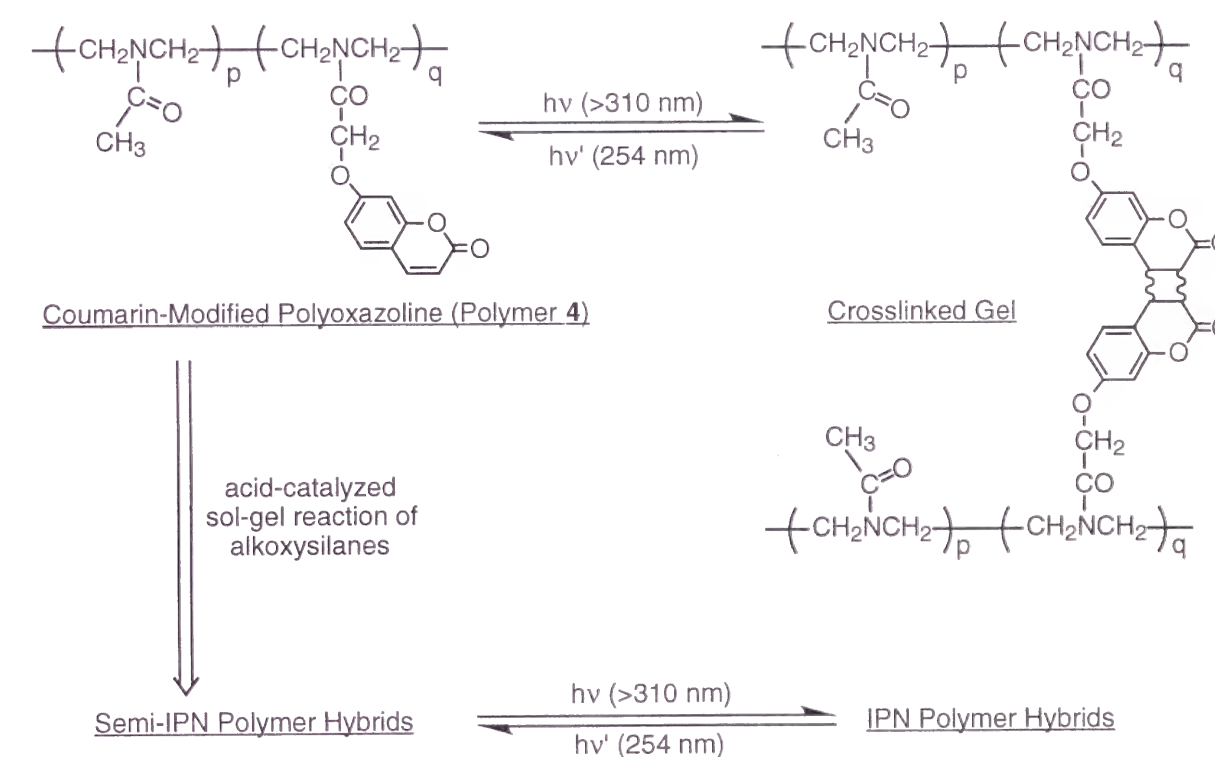
Interpenetrating polymer networks, IPNs, are a part of polymer blends where two or more polymers are combined, with at least one of the polymers crosslinked in the presence of the other(s). They are known to have distinct morphology and to exhibit properties different from only a sum of the original polymers or polymer gels.<sup>1</sup> In a narrow sense, compositions where each and all the polymers form networks are called IPN. On the other hand, polymer blends where one polymer is crosslinked while another remains linear are defined as semi-IPN. Composite materials consist of organic polymers and inorganic silica gel can be considered as a kind of IPN materials.<sup>2,3</sup> In our laboratory, organic-inorganic polymer hybrids having IPN structure have been synthesized by the *in-situ* polymerization method.<sup>4,5</sup> In this method, the sol-gel reaction of alkoxy silanes and radical copolymerization of organic monomers (and crosslink agent) are conducted simultaneously *in-situ*. They showed high thermal and/or mechanical stability and solvent-resistant property.



Scheme 1.

This chapter presents another method for the preparation of organic-inorganic polymer hybrids with an IPN structure (Scheme 1). Organic polymers having pendant crosslinkable functional groups can form a three-dimensional polymer network (gel) by a crosslinking reaction. Furthermore, if the reaction is reversible in response to external stimuli, it becomes

possible to build the gel-structure reversibly. Coumarin derivative is known to photo-dimerize upon irradiation by ultraviolet light with wavelengths longer than 310 nm,<sup>6,7</sup> and the reverse reaction (photo-cleavage) proceeds by the light of shorter wavelengths than 310 nm.<sup>8-10</sup> Poly(2-methyl-2-oxazoline) with pendant coumarin groups (**4**) has been prepared and its reversible gel-formation was reported previously.<sup>11</sup> In the present study, the preparation of organic-inorganic polymer hybrids from polymer **4** and the reversible photo-crosslinking reaction in the polymer hybrids are described (Scheme 2). The polymer hybrids form semi-IPN structure and IPN structure reversibly by the irradiation of light with different wavelengths. Changes in spectroscopic, thermal, and solvent-resistant properties were investigated.



Scheme 2.



## Experimental Section

### Materials

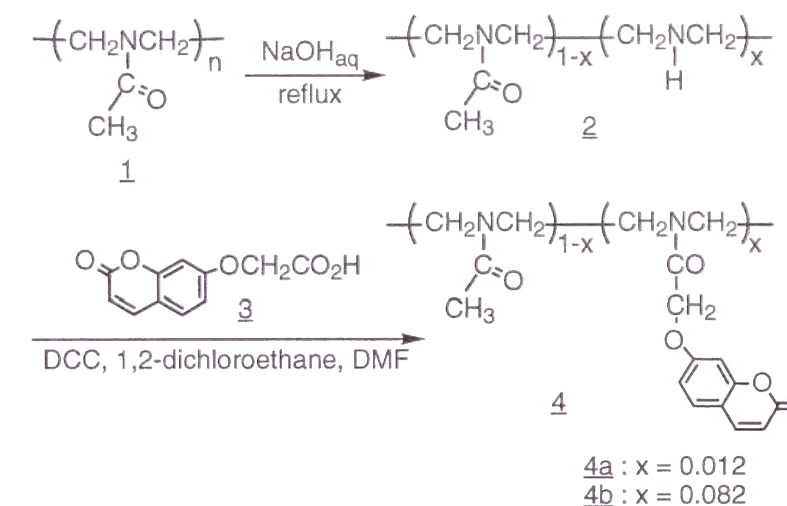
Tetramethoxysilane (TMOS), methyltrimethoxysilane (MeTMOS), and phenyltrimethoxysilane (PhTMOS) were distilled and stored under nitrogen atmosphere. Methanol was dried and distilled from magnesium methoxide, and stored under nitrogen atmosphere. Aqueous hydrochloric acid of various concentrations and DMF were used as received.

### Measurements

$^1\text{H}$ -NMR spectra were recorded on a 270MHz JEOL-JNM-GX270 NMR spectrometer. Absorption spectra were obtained on a JASCO V-530 spectrophotometer. Differential scanning calorimetry (DSC) thermograms were obtained with a DSC200, Seiko Instruments Inc., with the heating rate of 15 °C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed on a Shimadzu DT-30.

### Preparation of Polymer Hybrids from Polymer (4)

Polymer **4** was prepared by the condensation reaction of 7-coumariloxycetic acid and partially hydrolyzed poly(2-methyl-2-oxazoline), as illustrated in Scheme 3. Details of synthetic procedure are described previously.<sup>11</sup> Number average molecular weight was about 8,500 and degree of modification was determined from  $^1\text{H}$ -NMR and absorption spectra. Two polymers with the different degree of modification were prepared (**4a** and **4b**). A typical procedure for the preparation of polymer hybrids from polymer **4** is as follows. Polymer **4** and TMOS were dissolved in methanol and aqueous hydrochloric acid was added. The resulting mixture was placed in a polypropylene mold covered with a paper towel and left in air at room temperature for 1 week and at 60 °C for another week. After complete removal of the solvent by evaporation, polymer hybrids were obtained as glassy solid.



Scheme 3.

### Photo-Dimerization and Photo-Cleavage Reactions

Polymer hybrid films for photochemical reactions were prepared by casting the reaction mixture on quartz substrates (10 mm × 45 mm). Ethylene glycol was added to the solution as a drying control chemical additive (DCCA) to prevent cracking.<sup>12</sup> The cast films were placed at room temperature for several days, heated at 60 °C for 12 hours, and then heated at 80 °C under reduced pressure for 1 hour. No cracks were observed on the films. Film thickness was ca. 100 μm. Films of polymer **4a** and **4b** were also prepared on quartz substrates by casting the methanol solution of polymer. After removing the solvent by evaporation, the films were dried in vacuo at 70 °C for 12 hours.

Photo-dimerization of coumarin groups was induced by the irradiation of light longer than 310 nm by a 450W high-pressure mercury lamp through a pylex cooler. Photo-cleavage reaction was carried out by the irradiation at 254 nm by a 10W low-pressure mercury lamp. Both reactions were performed at room temperature, and followed by the absorption spectra.

### Solvent-Resistant Property of Polymer Hybrids

Polymer hybrids were ground in a mortar and the resulting powders were extracted

with methanol by using Soxhlet apparatus for 1 week, or stirred in DMF for 1 week. The quantity of the organic component remaining in the polymer hybrids after extraction was evaluated from the elemental analysis of nitrogen and the thermogravimetric analysis in air.

## Results and Discussion

### *Synthesis of Polymer Hybrids*

Table 1 summarizes the results of the preparation of the polymer hybrids from polymer **4**. Methanol was used as a solvent and three kinds of alkoxysilanes were employed. The effect of acid concentration was also examined. It was found that the higher acid concentration gave the higher homogeneity of the polymer hybrids when TMOS was used as the alkoxysilane (runs 1-4). And with 1 molar hydrochloric acid, transparent and homogeneous polymer hybrids could be obtained in a wide range of the feed ratios of **4a** to TMOS (runs 4-8). On the contrary, it was difficult to obtain homogeneous polymer hybrids with MeTMOS and PhTMOS (runs 13-19).

These results are somewhat different from the previous study with poly(2-methyl-2-oxazoline) (**1**), where the transparent material could be obtained easily not only with TMOS but with MeTMOS and PhTMOS.<sup>13</sup> Only 1.2 mol% modification of **1** with coumarin group largely affected the homogeneity of the polymer hybrids. This may be attributed to the hydrophobicity of the coumarin moieties. Polymer **4** dissolves well in methanol in the first stage of the reaction. It is considered that the low homogeneity of the resulting polymer hybrids is the result of the aggregation of coumarin groups during the sol-gel reaction and the evaporation of methanol due to their hydrophobicity. The sol-gel reaction of alkoxysilanes, that is, the hydrolysis and the condensation reactions, is accelerated with higher acid concentration. Consequently, the gelation took place faster. This acceleration effect allows the reaction mixture to be frozen before macroscopic phase separation, and the homogeneous polymer hybrids could be obtained only with 1 molar hydrochloric acid. The low homogeneity with MeTMOS and PhTMOS can be explained by slower gelation with tri-functional MeTMOS and PhTMOS than tetra-functional TMOS. It seems that the tendency of aggregation of coumarin also causes high yield of the photodimerization of coumarin in the polymer hybrids. This will be discussed in later section.

**Table 1.** Organic-Inorganic Polymer Hybrids from Polymer **4**.<sup>a</sup>

run	polymer <sup>b</sup>	alkoxysilane	weight ratio <sup>c</sup>	HCl <sub>aq</sub> <sup>d</sup>	appearance
1	<b>4a</b>	TMOS	1/20	10 <sup>-3</sup> M	turbid
2	<b>4a</b>	TMOS	1/20	10 <sup>-2</sup> M	translucent
3	<b>4a</b>	TMOS	1/20	10 <sup>-1</sup> M	translucent
4	<b>4a</b>	TMOS	1/20	1 M	transparent
5	<b>4a</b>	TMOS	1/10	1 M	transparent
6	<b>4a</b>	TMOS	1/4	1 M	transparent
7	<b>4a</b>	TMOS	1/2	1 M	transparent
8	<b>4a</b>	TMOS	1/1	1 M	transparent
<hr/>					
9	<b>4b</b>	TMOS	1/20	1 M	transparent
10	<b>4b</b>	TMOS	1/10	1 M	transparent
11	<b>4b</b>	TMOS	1/4	1 M	phase separated
12	<b>4b</b>	TMOS	1/2	1 M	phase separated
<hr/>					
13	<b>4a</b>	MeTMOS	1/20	10 <sup>-3</sup> M	turbid
14	<b>4a</b>	MeTMOS	1/20	10 <sup>-2</sup> M	translucent
15	<b>4a</b>	MeTMOS	1/20	10 <sup>-1</sup> M	turbid
16	<b>4a</b>	MeTMOS	1/20	1 M	translucent
<hr/>					
17	<b>4a</b>	PhTMOS	1/20	10 <sup>-2</sup> M	phase separated
18	<b>4a</b>	PhTMOS	1/20	10 <sup>-1</sup> M	translucent
19	<b>4a</b>	PhTMOS	1/20	1 M	translucent

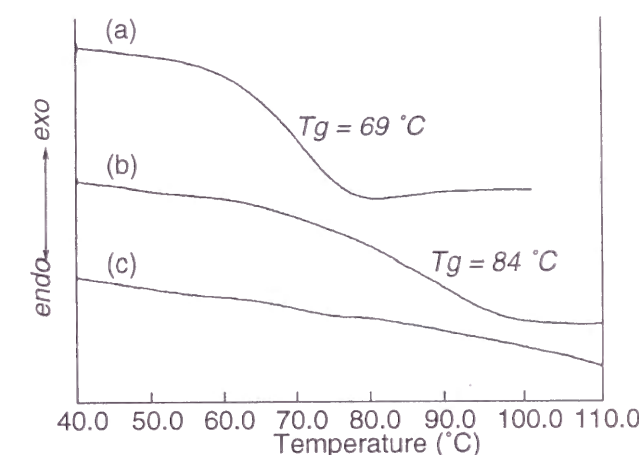
<sup>a</sup> alkoxysilane 1 g, methanol 10 ml, at r.t. in air. <sup>b</sup> **4a** : coumarin content 1.2 mol%, **4b** : coumarin content 8.2 mol%. <sup>c</sup> feed ratio of polymer to alkoxysilane (w/w). <sup>d</sup> 4 eq. to TMOS, 3 eq. to MeTMOS and PhTMOS.

Preparation of polymer hybrids from higher coumarin-content polymer **4b** (8.2 mol%) was also examined (runs 9-12). Transparent polymer hybrids could be obtained only with lower polymer ratio, and higher polymer ratio brought about the phase separation. The effect of aggregation of coumarin groups should dominate in these cases.

Usually many cracks appeared in the polymer hybrids from TMOS. They could be avoided by adding ethylene glycol to the reaction mixture as a drying control chemical

additive,<sup>12</sup> and crackless films were prepared on quartz substrates. In the following section these films were used to investigate the reversible photo-dimerization reactions of the coumarin groups in the polymer hybrids spectroscopically.

Glass transition behaviors of polymer **4** and the polymer hybrids were studied using differential scanning calorimetry (DSC). Figure 1 shows representatively the DSC thermograms of polymer **4b** and polymer hybrid from **4b** (run 10). Glass transition temperature (T<sub>g</sub>) of **4b** was observed at 69 °C (Figure 1a). On the other hand, as shown in Figure 1c, glass transition was not distinguished in the DSC thermogram of the polymer hybrid. This observation indicates that polymer **4** is dispersed at the molecular level in silica gel network.

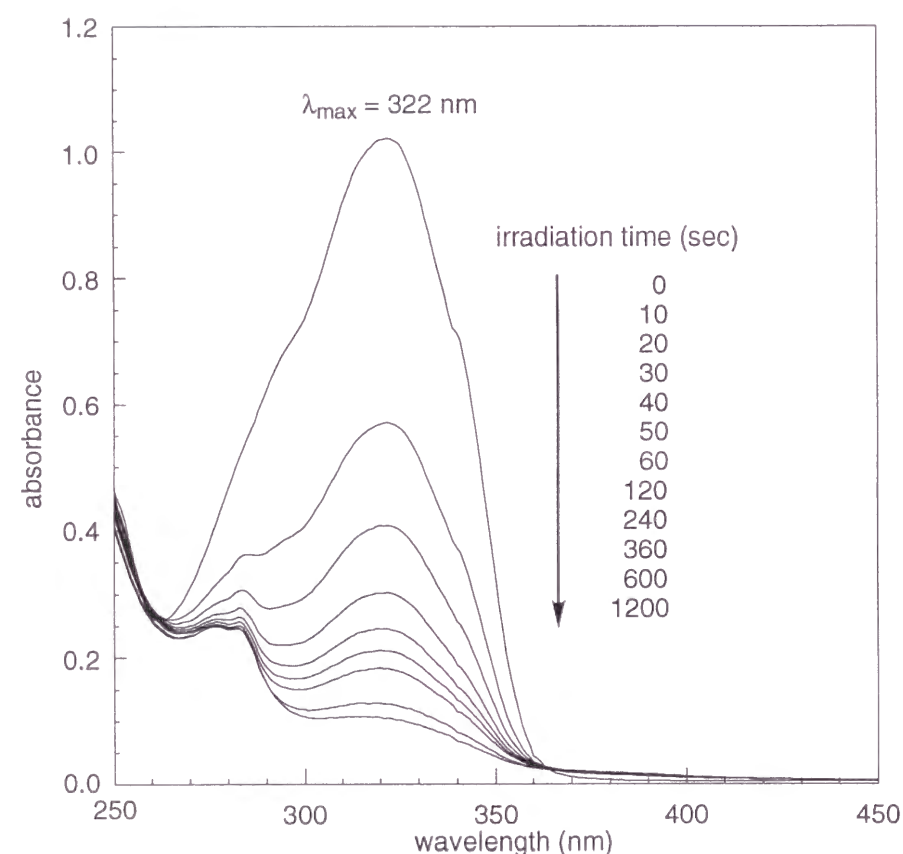
**Figure 1.** DSC thermograms of (a) polymer **4b** before the crosslink, (b) polymer **4b** after the crosslink, and (c) polymer **4b**/TMOS polymer hybrid (run 10).

### Photo-Dimerization of Coumarin Groups in the Polymer Hybrids

The photo-dimerization of the coumarin groups was induced by the light of longer wavelengths than 310 nm by a high-pressure mercury lamp. The reaction was carried out on all the transparent polymer hybrid films (runs 4-10) as well as the films of polymer **4a** and **4b**. Almost quantitative reaction was confirmed by absorption spectra in all the samples.



Figure 2 shows the typical change of the absorption spectra of polymer hybrid film upon the irradiation. Decline of the absorption at 322 nm indicates the progress of photo-dimerization and the formation of IPN structure in the polymer hybrids. The reaction took place almost quantitatively even with the lowest coumarin content sample (run 4), suggesting that the coumarin groups exist adjacent to each other in the polymer hybrids. This corroborates the aggregation of the coumarin groups in the polymer hybrids, which was presumed from the results of the preparation of the polymer hybrids. No change was found in the appearance of the polymer hybrid films during the irradiation.



**Figure 2.** The change of absorption spectra of the polymer hybrid (run 6) upon irradiation of light longer than 310 nm by a 450W high-pressure mercury lamp.

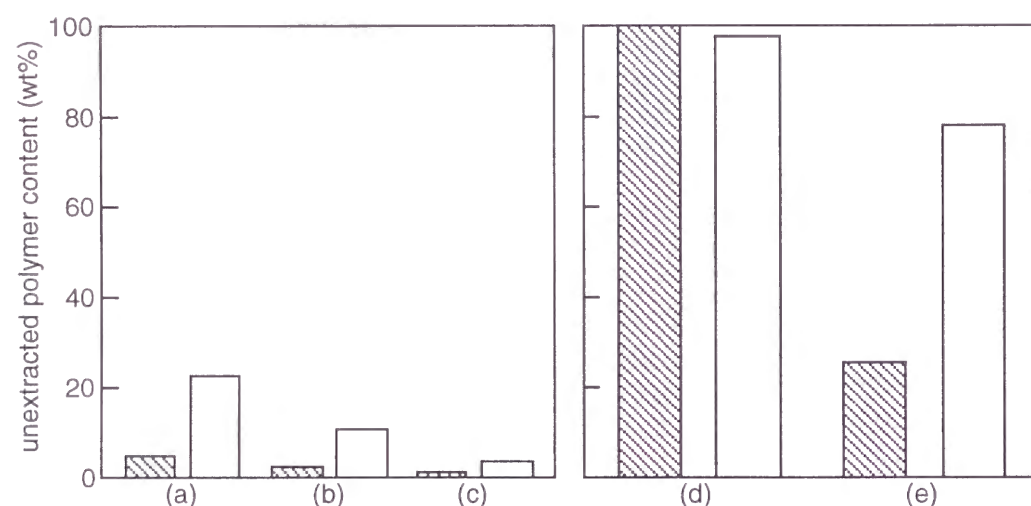
### Thermal and Solvent-Resistant Properties of Polymer Hybrids

T<sub>g</sub> of polymer **4b** rose from 69 °C to 84 °C and the transition became broader after the photo-dimerization (Figure 1a and 1b). In other words, the photo-dimerization, namely, the crosslink of the polymer main chain, affected the thermal property of the polymer. On the other hand, as polymer **4** is dispersed completely in the polymer hybrids, it is difficult to expect any change of thermal property of the polymer hybrids by the crosslink. Glass transition was hardly observed by DSC on all the transparent polymer hybrids (runs 4-10), as representatively shown in Figure 1c (run 10). Thermogravimetric analysis (TGA) study was also carried out, but no remarkable change of thermal stability was found. The crosslink of polymer **4** seems to have little effect on the thermal properties of the polymer hybrids.

Solvent-resistant property is another interest, as the IPN polymer hybrids have been found to have excellent solvent-resistant property compared with the traditional ones.<sup>14</sup> The solvent-resistant properties of the polymer hybrids before and after the crosslink were compared with each other from remained polymer contents after extraction with methanol or DMF. Left side graph of Figure 3 (a-c) shows the results of the extraction experiment on the polymer hybrids from low-coumarin-content polymer **4a**. Solvent-resistant property seems to be improved by the crosslink in all the samples. Most of the organic polymer was, however, extracted with methanol even after the crosslink. It is considered that the crosslink density is too small to prevent the extraction. This is supported by the fact that the polymer **4a** dissolves in methanol even after the complete crosslink.

On the contrary, in the case of the polymer hybrids from high-coumarin-content polymer **4b**, organic component was hardly extracted with methanol even before the crosslink (Figure 3(d)). Generally, as exemplified in the case of the polymer hybrids from polymer **4a**, linear polymer can easily be extracted from polymer hybrids by hydrogen-bond donating solvents like methanol. There are two possibilities to explain this unusual solvent-resistant behavior of uncrosslinked polymer hybrids from **4b**. One is that the lactone ring of coumarin group is hydrolyzed in acidic reaction media, and forms covalent bond with silica matrix through

condensation between silanol groups on silica gel and generated alcohol or carboxylic acid groups.

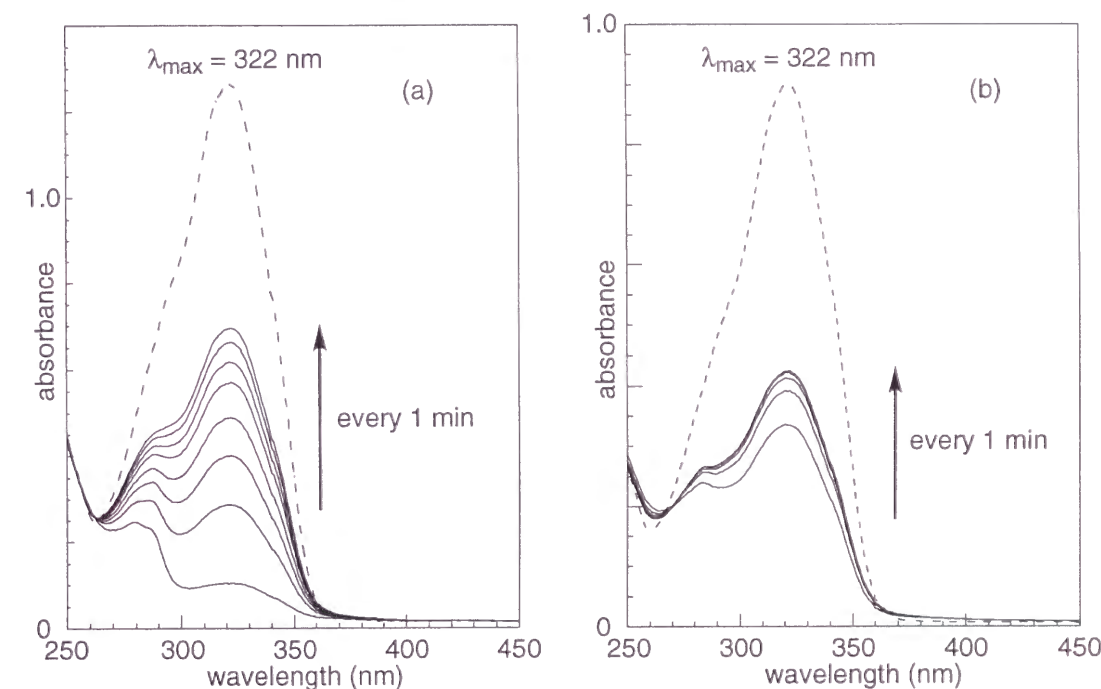


**Figure 3.** Solvent-resistant property of the polymer hybrids from polymer **4a** (a-c) and **4b** (d,e). Shaded and white columns are the unextracted polymer contents before and after the crosslink reaction, respectively. (a) run 5 (**4a**/TMOS = 1/10), extracted with methanol; (b) run 6 (1/4), with methanol; (c) run 7 (1/2), with methanol; (d) run 10 (**4b**/TMOS = 1/10), with methanol; (e) run 10, with DMF.

Another possibility is that the main chain of polymer **4b** is physically linked by the aggregates of coumarin groups. As described in the previous sections, the coumarin groups are supposed to aggregate to some extent in the polymer hybrids owing to their hydrophobicity. Polymer **4b** itself dissolves in methanol, but in the polymer hybrids polymer **4b** is surrounded by rigid silica matrix and polymer must move through the pores of silica in order to be extracted. In such a fixed state, the coumarin aggregates can not be broken by methanol and act as the physically crosslinking points. If the latter is the case, polymer **4b** might be extracted by using DMF as a solvent, since DMF is thought to be a better solvent for both coumarin groups and polymer main chain. Actually, as shown in Figure 3(e), 73 wt% of the organic component was extracted by DMF before the crosslink. This indicates that polymer **4b** was not covalently linked to the silica matrix, but a kind of physical crosslink might occur. After the photo-crosslinking of polymer **4b**, the extracted content was suppressed to be ca. 20 wt%.

Improvement of the solvent-resistant property by the formation of the IPN structure was confirmed.

In this system, both the inter- and intra-chain photo-dimerizations are able to occur. As a result, although the photo-dimerization was quantitative, the crosslink density should be smaller than the degree of modification (8.2 mol%). Consequently some of the polymers were extracted even after the crosslink. It was difficult, however, to determine the ratio of the inter-/intra-chain reactions.



**Figure 4.** The change of absorption spectra during the photo-cleavage reaction induced by irradiation at 254 nm: (a) polymer **4b** gel, (b) polymer hybrid (run 10).

#### Photo-Cleavage (Reverse Photo-Dimerization) Reaction in the Polymer Hybrids

The cyclobutane ring of the coumarin dimer is known to be cleaved by the irradiation of light shorter than 310 nm.<sup>8-10</sup> The crosslinked polymer **4b** film was subjected to photo-cleavage reaction by the irradiation at 254 nm using a low-pressure mercury lamp. Figure 4(a) shows



the change of the absorption spectra of the crosslinked polymer **4b** film upon irradiation. The absorption at 322 nm increased gradually. This result meant that the photo-cleavage reaction did occur and the original coumarin groups were regenerated. The absorption intensity, however, did not completely recover after a long-time irradiation. Conversion of the photo-cleavage reaction was calculated from the absorption spectra to be 62 %. The reaction proceeded in all the polymer hybrid films in the same way, and about 16 % of the coumarin dimer was converted to the original monomer. Figure 4(b) shows the typical change of the absorption spectra upon irradiation on the polymer hybrid film (run 10). There are several possibilities to explain the low photo-cleavage efficiency, that is, the re-photo-dimerization by 254 nm light, the photo-decomposition of coumarin ring, or the formation of stable photo-dimer upon the irradiation by the high-pressure mercury lamp.<sup>15, 16</sup> However, the reason has not been clarified yet.

### Conclusion

Organic-inorganic polymer hybrids were prepared from coumarin-modified polyoxazoline **4** with various coumarin contents. Transparent and homogeneous polymer hybrids were obtained with TMOS as an alkoxysilane. Acceleration of sol-gel reaction by employing 1 molar hydrochloric acid as an acid catalyst was important to obtain homogeneous polymer hybrids. Photo-dimerization of coumarin groups in the polymer hybrids took place almost quantitatively even with the lowest polymer ratio sample. These results were due to the tendency of the coumarin groups to aggregate in the reaction mixture. The solvent-resistant property of the polymer hybrids was found to be improved by the formation of IPN structure. This new strategy to prepare the IPN polymer hybrids can be applied to other polymers having other crosslinkable side groups.

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## Chapter 4

### Photochemically Reversible IPN Polymer Hybrids Utilizing the Photodimerization of Thymine

#### Abstract

Formation of an interpenetrating polymer network (IPN) composed of organic polymer gel and silica gel in the form of polymer hybrids was conducted by utilizing the photodimerization of thymine bases. Thymine-modified poly(2-methyl-2-oxazoline) (POZO-T) was synthesized by the condensation reaction of partially hydrolyzed polyoxazoline and 1-(2-carboxyethyl)thymine. Organic-inorganic polymer hybrids were prepared from POZO-T and tetramethoxysilane (TMOS). Transparent and homogeneous polymer hybrids could be obtained. The photodimerization and the reverse reaction of thymine in the polymer hybrids were monitored by the UV absorption spectroscopy.

## Introduction

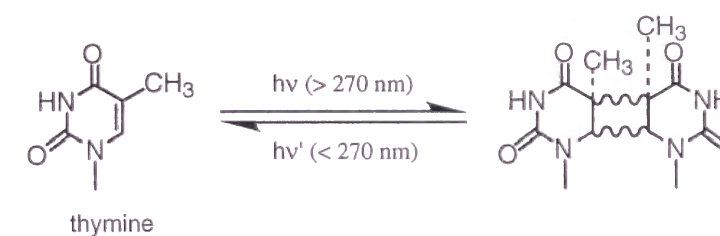
Organic polymers having strong hydrogen bond accepting groups, e.g., amide or urethane, can be dispersed homogeneously at a molecular level in a silica gel matrix by the sol-gel reaction of alkoxysilanes.<sup>1-4</sup> Poly(2-methyl-2-oxazoline), poly(*N*-vinylpyrrolidone), and poly(*N,N*-dimethylacrylamide) are representatives of such polymers. The hydrogen bonding interactions between the silanol groups generated by the hydrolysis of alkoxysilane<sup>5</sup> and the hydrogen bond accepting groups in organic polymers are crucial for the formation of single-phase nanocomposites.

In these polymer hybrids, linear organic polymers are embedded in a three-dimensional silica network. This kind of structure is classified as a *semi*-interpenetrating polymer network (IPN).<sup>6</sup> On the contrary, if both organic and inorganic phases are three-dimensionally crosslinked and they are interpenetrated each other, it is a *complete* IPN.<sup>6</sup> Novak *et al.* have obtained a kind of IPN organic-inorganic nanocomposites via the synchronous formation of both the inorganic and organic components.<sup>7,8</sup> This was accomplished by the sol-gel reaction of tetraalkenyl orthosilicates to form an inorganic SiO<sub>2</sub> matrix while simultaneously eliminating unsaturated alcohols which are polymerized *in-situ* using free-radical or metathesis techniques. A small amount of divinyl monomers was added to the reaction mixture prior to polymerization in order to crosslink the organic component. Chujo *et al.* have also proposed two methodologies to prepare the IPN polymer hybrids. One is by the *in-situ* polymerization method.<sup>9-13</sup> The radical copolymerization of *N,N*-dimethylacrylamide or styrene and bifunctional crosslink agents was carried out simultaneously *in-situ* with the sol-gel reaction of alkoxysilane. The resulting IPN polymer hybrids showed excellent solvent resistance.<sup>9,10</sup> The other is to introduce reactive functional groups in the side chain of organic polymers.<sup>14,15</sup> The polymer hybrids prepared from these preformed polymers possess *semi*-IPN structure. The crosslinking reaction of organic polymers was then conducted by the photodimerization reaction of coumarin groups<sup>14</sup> or the Diels-Alder reaction of maleimide and furan groups.<sup>15</sup> The reactions employed here were reversible, that is, the reproduction of coumarin groups or retro-Diels-Alder reaction

was possible.

In this chapter, the photodimerization of thymine bases was utilized to achieve the reversible IPN polymer hybrids. Thymine bases are known to photodimerize upon the irradiation above 270 nm and revert back to be thymine again upon the irradiation below 270 nm (Scheme 1).<sup>16-20</sup> In the case of coumarin, although the photodimerization reaction of coumarin in the polymer hybrids was found to be almost quantitative, the reproduction of coumarin upon the irradiation at 254 nm was not complete. It is expected that the reversible photodimerization of thymine bases accomplishes the improved reversibility.

Thymine bases were introduced in the side chain of poly(2-methyl-2-oxazoline)s (POZO-T), and the polymer hybrids were prepared from POZO-T and tetramethoxysilane. Reversible dimerization of thymine bases in the polymer hybrids was monitored by UV absorption spectroscopy.



**Scheme 1.** Photocycloaddition reaction of thymine.

## Experimental Section

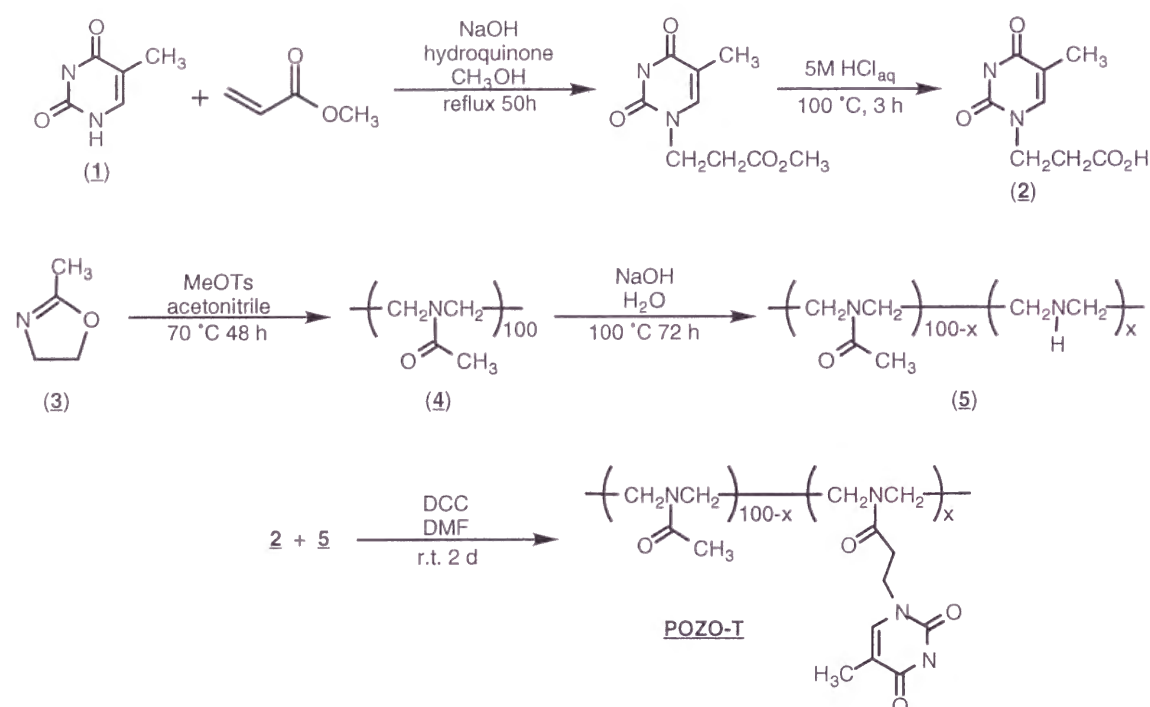
### General Procedure

<sup>1</sup>H-NMR spectra were recorded using a 270MHz JEOL-JNM-GX270 NMR spectrometer. Absorption spectra were obtained using a JASCO V-530 spectrophotometer. Thermogravimetric analysis (TGA) was performed using a TG/DTA6200, SEIKO Instruments, Inc., with a heating rate of 10 °C min<sup>-1</sup> in air.



### Materials

Methyl acrylate was distilled under reduced pressure. Methanol was dried and distilled from magnesium methoxide and stored under nitrogen atmosphere. 2-Methyl-2-oxazoline was dried and distilled from KOH and stored under nitrogen. Methyl *p*-toluenesulfonate (MeOTs) was distilled under reduced pressure and stored under nitrogen. Acetonitrile was dried and distilled from CaH<sub>2</sub> and stored under nitrogen. Tetramethoxysilane (TMOS) was distilled and stored under nitrogen. Other chemicals are all used as received.



**Scheme 2.** Synthetic route of thymine-modified poly(2-methyl-2-oxazoline)s (POZO-T).

### Synthesis of Thymine-Modified Poly(2-methyl-2-oxazoline)s (POZO-T)

The synthetic route of POZO-T is shown in Scheme 2. 1-(2-Carboxyethyl)thymine (2) was prepared according to the literature.<sup>20</sup> Poly(2-methyl-2-oxazoline) (4) was prepared by the ring-opening polymerization of 2-methyl-2-oxazoline (3) initiated by MeOTs.<sup>21</sup> The feed ratio of monomer to initiator was set to be 100 ( $M_n = 8,500$ ). Partial hydrolysis of polymer 4

in alkaline condition gives secondary amine unit in the main chain (5).<sup>22</sup> The degree of hydrolysis was calculated from <sup>1</sup>H NMR data to be 11.0 mol%. The condensation reaction of 2 and 5 gives POZO-T. <sup>1</sup>H NMR spectrum of POZO-T is shown in Figure 1. Assignment of each peak is illustrated in the figure. The UV absorption spectrum of POZO-T in methanol is shown in Figure 2.

### Preparation of Polymer Hybrids from POZO-T

POZO-T and TMOS were dissolved in methanol and aqueous hydrochloric acid (4 equivalents to TMOS) was added. The resulting mixture was stirred in a sealed bottle for 1 h before allowing the solvent to evaporate in air. After gelation and removal of the solvent, the polymer hybrids were obtained as glassy solids. Polymer contents were determined from TGA analysis. Polymer hybrid films for absorption measurement were prepared on quartz substrates by casting the reaction mixture.

### Photo-Dimerization and Photo-Cleavage Reactions

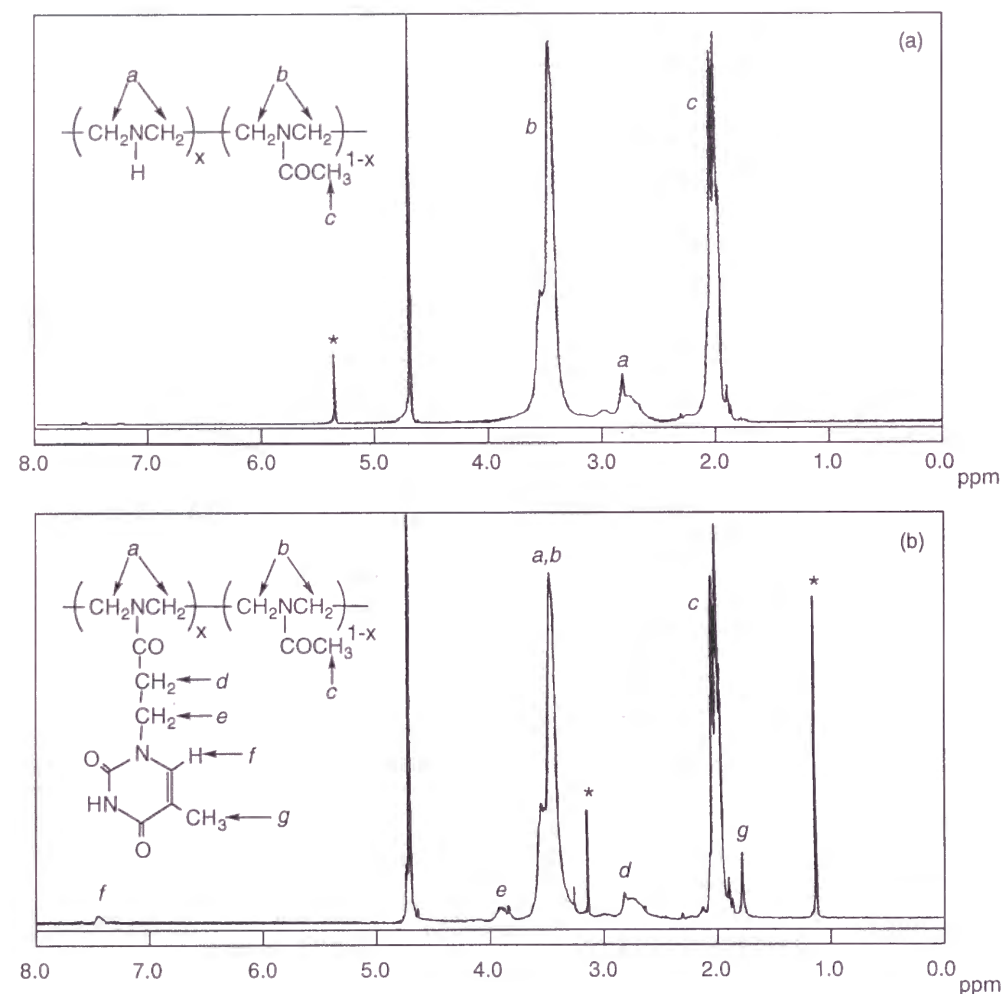
Photo-dimerization of thymine groups was induced by the irradiation of light from 175W Xe lamp filtered with a Toshiba UV-D33S glass filter. Photo-cleavage reaction was carried out by the irradiation at 254 nm by a 10W low-pressure mercury lamp. Both reactions were performed at room temperature, and followed by the absorption spectroscopy.

### Solvent Extraction

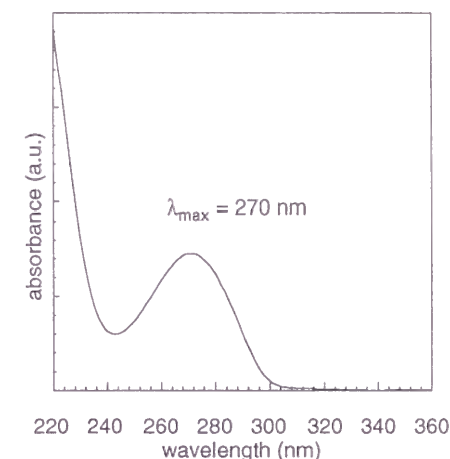
Polymer hybrids were ground in a mortar and the resulting powders were extracted with methanol by using Soxhlet apparatus for 1 week, or stirred in DMF for 1 week. The quantity of the organic component remaining in the polymer hybrids after extraction was evaluated from TGA in air.

## Results and Discussion

Thymine-modified poly(2-methyl-2-oxazoline)s (POZO-T) were successfully synthesized by the condensation reaction of partially hydrolyzed poly(2-methyl-2-oxazoline) (**5**) and 1-(2-carboxyethyl)thymine (**2**) with DCC as an activating agent. Figure 1 shows the  $^1\text{H}$  NMR spectra of the partially hydrolyzed polyoxazoline (a) and the corresponding POZO-T (b).



**Figure 1.**  $^1\text{H}$  NMR spectra of (a) partially hydrolyzed poly(2-methyl-2-oxazoline) and (b) corresponding POZO-T (solvent  $\text{D}_2\text{O}$ ). \* depicts solvent contaminate.



**Figure 2.** UV absorption spectrum of POZO-T in methanol.

From the integral ratio of methylene protons adjacent to *N*-acetyl amide and secondary amine in Figure 1(a), the degree of hydrolysis was estimated to be 11.0 mol%. In Figure 1(b), new peaks corresponding to thymine moiety were observed (peaks *d*, *e*, *f*, *g*) and methylene protons adjacent to secondary amine group decreased. The degree of introduction of thymine groups calculated from Figure 1(b) was 10.6 mol%. The reaction efficiency of secondary amine on the polymer (**4**) and thus the degree of introduction of thymine groups was found to be almost quantitative from  $^1\text{H}$  NMR data. Figure 2 shows the UV absorption spectrum of POZO-T. The absorption band at the maximum wavelength of 270 nm is originated from thymine moiety.

Polymer hybrids were prepared by the acid-catalyzed sol-gel reaction of TMOS in the presence of POZO-T. The results are summarized in Table 1. It was found that higher homogeneity was achieved by employing higher acid concentration (compare runs 2 and 3) and smaller amount of solvent (compare runs 4 and 5). Transparent polymer hybrids with polymer content as much as 67 wt% could be obtained by choosing appropriate conditions. Thymine moiety has rather poor miscibility in the reaction mixture and tends to aggregate.

The tendency of aggregation of thymine moiety could be overcome by controlling the acid concentration and the amount of solvent. Both high acid concentration and small amount of solvent cause acceleration of the sol-gel reaction and hence faster gelation. This allows the better dispersion of thymine. The same trend was observed in the preparation of polymer hybrids from coumarin-modified polyoxazolines.<sup>14</sup>

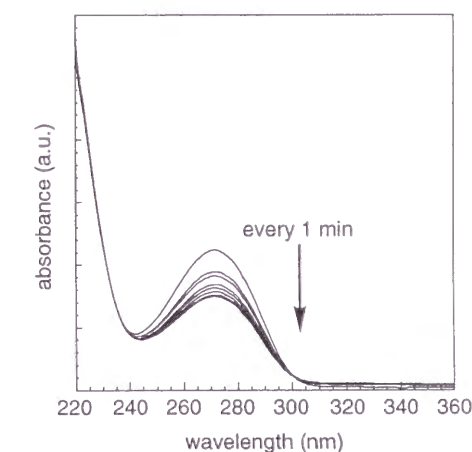
**Table 1.** Preparation of polymer hybrids from POZO-T.

run	POZO-T (mg)	TMOS (mg)	CH <sub>3</sub> OH (mL)	HCl <sub>aq</sub> <sup>a</sup>	appearance	polymer content (wt%)	
						calcd.	obsd. <sup>b</sup>
1	50	1,000	5	0.1 M	transparent	-	-
2	50	500	5	0.1 M	translucent	-	-
3	50	500	5	1 M	transparent	20.0	26.5
4	100	500	10	1 M	translucent	-	-
5	100	500	1	1 M	transparent	33.3	39.5
6	100	250	10	1 M	turbid	-	-
7	100	250	1	1 M	transparent	50.0	50.2
8	100	125	1	1 M	transparent	66.7	67.0

<sup>a</sup> Concentration of aqueous hydrochloric acid. <sup>b</sup> Polymer contents in the polymer hybrids were calculated from TGA by charring the sample up to 900 °C in air.

Photoirradiation on the polymer hybrids was then carried out to induce the photodimerization of thymine. The films of polymer hybrids were prepared on quartz substrates. The changes of UV absorption during the photoirradiation were monitored. The absorption at 270 nm declined gradually, indicating the progress of photocycloaddition of thymine. A typical change of absorption spectra during the irradiation is shown in Figure 3. The reaction was saturated within 20 minutes. The photocycloaddition efficiencies estimated from the UV absorption spectra are listed in Table 2. Apparently the efficiencies in the polymer hybrids decreased with higher silica content. In the previous study of the polymer hybrids where coumarin-modified polyoxazolines were used instead of POZO-T,<sup>14</sup> the photodimerization of coumarin took place quantitatively, even in the polymer hybrid whose polymer content was lower than 10 wt%. The lower photodimerization efficiency in the present POZO-T hybrid

suggests that the less number of thymine groups are close enough to photodimerize. It is considered that this low efficiency is due to the hydrophilic nature of thymine group compared to coumarin group. It was found, however, that quite high efficiency around 80% was observed in the polymer hybrids whose polymer content was 50% (run 7). This dimerization efficiency is high enough to improve the solvent resistance of the polymer hybrid.



**Figure 3.** The change of absorption during irradiation of the polymer hybrid (run 5 in Table 1. POZO-T/silica=1/1).

**Table 2.** Reaction efficiency of photocycloaddition.

sample	efficiency (%)
run 3 (POZO-T:silica=1:4) hybrid	24.0
run 5 (POZO-T:silica=1:2) hybrid	36.4
run 7 (POZO-T:silica=1:1) hybrid	79.9
run 8 (POZO-T:silica=2:1) hybrid	80.8
POZO-T film	94.0
POZO-T:polyoxazoline (1:1) blend	86.8

To clarify the reason of the decline of the photodimerization efficiency in the polymer hybrids, a film of polymer blend composed of POZO-T and poly(2-methyl-2-oxazoline) (**4**) (1/1, w/w) were prepared. The efficiency of the photodimerization in the blend film was



found to be 87%, which is lower than that of pure POZO-T film but higher than that of the polymer hybrid which has similar POZO-T content (run 7). This result indicates that the decline of the photodimerization efficiency in the polymer hybrids can partly be explained from a decrease of thymine concentration in the polymer hybrids. Additionally, the other reasons such as the rigidity or the acidity of the silica matrix should be considered.

Investigation on the photocleavage of thymine dimer was carried out by the irradiation at 254 nm from a low-pressure mercury lamp. It was found that ca. 17 % of thymine dimer was converted to thymine monomer upon the irradiation. The progress of the photocleavage was, however, hardly observed in the polymer hybrids.

## Conclusions

IPN polymer hybrids were prepared from thymine-modified polyoxazoline (2). Transparent and homogeneous polymer hybrids could be obtained by choosing the concentration of acid catalyst and the amount of solvent. The progress of the photodimerization of thymine in the polymer hybrids was confirmed by UV absorption spectroscopy. Unfortunately, the reverse reaction hardly took place upon the irradiation from a low-pressure mercury lamp at 254 nm.

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## **Part II**

### **Thermo-Responsive Organic-Inorganic Polymer Hybrids**

## Chapter 5

### Thermally Reversible IPN Polymer Hybrids Utilizing the Diels-Alder Reaction

#### Abstract

Formation of an IPN (interpenetrating polymer network) of organic polymer and silica gel in the form of polymer hybrids was accomplished by utilizing Diels-Alder reaction between maleimide and furan. Maleimide and furan groups were introduced in the side chain of poly(2-methyl-2-oxazoline), respectively. Polymer hybrids were prepared by acid-catalyzed sol-gel reaction of tetramethoxysilane (TMOS) in the presence of these polymers. The progress of the Diels-Alder reaction between maleimide and furan was confirmed by UV and FT-IR spectroscopy. The solvent resistance of the polymer hybrids was improved by the formation of the IPN structure. Retro-Diels-Alder reaction takes place at elevated temperature, and these reactions can be cycled.



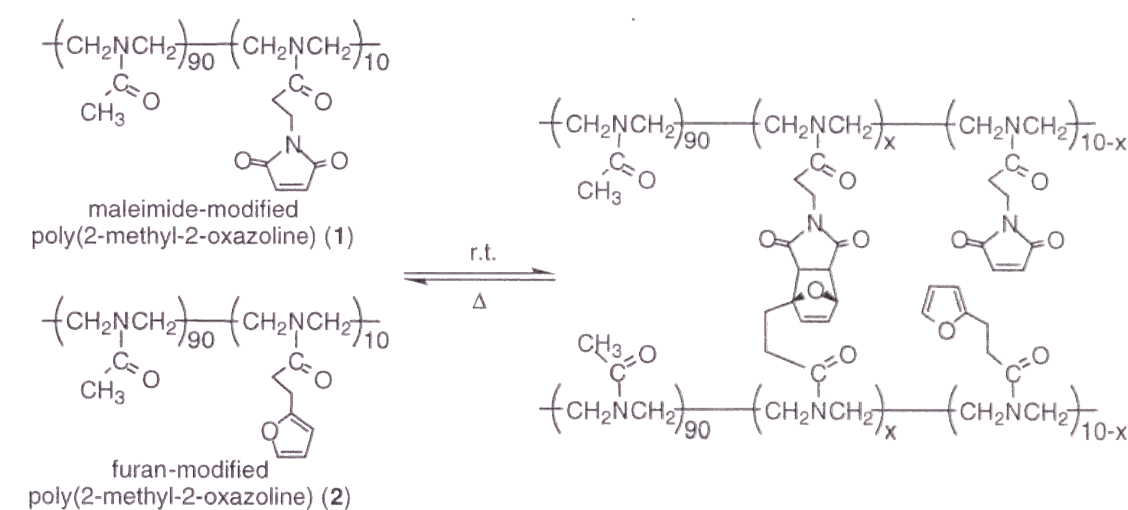
## Introduction

Preparation of nanocomposites of organic polymers and silica gel has been achieved by the sol-gel reaction of alkoxysilanes in the presence of organic polymers.<sup>1-4</sup> The sol-gel reaction involves the hydrolysis of Si-OR groups to Si-OH (silanol) groups and the condensation of the Si-OH groups into -Si-O-Si- linkages.<sup>5</sup> Generally, the nano-dispersion of organic components in a silica matrix can be accomplished either (i) by the formation of covalent bond between organic components and silica, or (ii) through weak interactions (hydrogen bonding, aromatic interaction, ionic interaction, and so on) between them. Organic polymers such as poly(2-methyl-2-oxazoline) and poly(*N*-vinylpyrrolidone) were incorporated into a silica network, utilizing the hydrogen bonding interaction between the silanol groups and the amide groups of the organic polymers.<sup>6,7</sup> Organic polymers are dispersed on the scale of a few nanometers in these hybrid materials.

In the polymer hybrids, a linear polymer is embedded in the three-dimensionally cross-linked silica network. This kind of structure is called a "semi-interpenetrating polymer network (*semi*-IPN)". On the contrary, if both organic and inorganic phases are cross-linked independently and they are interpenetrated each other, it is a *complete* IPN.<sup>8</sup> Organic-inorganic IPN nanocomposites were prepared by Novak *et al.* via the synchronous formation of both the inorganic and organic components.<sup>9,10</sup> This was accomplished by the sol-gel reaction of tetraalkoxysilanes possessing polymerizable alkoxides. The hydrolysis and condensation of the alkoxysilanes to form an inorganic silica network liberate unsaturated alcohols which are polymerized *in-situ* using free-radical or metathesis techniques. A small amount of divinyl monomers was added to the reaction mixture prior to polymerization in order to cross-link the organic polymer. IPN nanocomposites thus prepared showed greater moduli than *semi*-IPN ones. Chujo *et al.* proposed two methodologies to prepare the IPN polymer hybrids. One is called the "*in-situ* polymerization method", where the radical copolymerization of mono- and difunctional vinyl monomers and the sol-gel reaction of alkoxysilanes are carried out simultaneously *in-situ*.<sup>11-13</sup> The other is the preparation of polymer hybrids from preformed

organic polymers having pendant cross-linkable functional groups. The hybrid prepared from the cross-linkable prepolymer is *semi*-IPN, while it is converted to IPN by the cross-link reaction of the polymers. Especially, it is quite interesting when a reversible bond-forming reaction is employed to cross-link organic polymers. Conversion between *semi*-IPN and IPN can be done by choosing the condition to promote either the bond-forming and bond-cleaving reactions. It is expected that the properties of the hybrids, e.g., mechanical property or solvent resistance, are modified by the formation of IPN. Reversible photo-dimerization of coumarin groups has been utilized to perform photochemically reversible formation of IPN in the polymer hybrids, and the modification of solvent resistance by light was achieved.<sup>14</sup>

This chapter describes the thermo-responsive formation of IPN polymer hybrids by utilizing Diels-Alder (DA) reaction of maleimide and furan. Reversible formation of hydrogel of poly(2-methyl-2-oxazoline) by means of DA reaction has been reported previously (Scheme 1).<sup>15</sup> DA reaction between maleimide group and furan group proceeds at ambient temperature and retro-DA reaction takes place on heating.<sup>16</sup> The preparation of the polymer hybrids, the efficiency of the DA and retro-DA reactions in the polymer hybrids, as well as their change in solvent resistance were investigated.



**Scheme 1.** Hydrogel from maleimide- and furan-modified poly(2-methyl-2-oxazoline)s.<sup>15</sup>

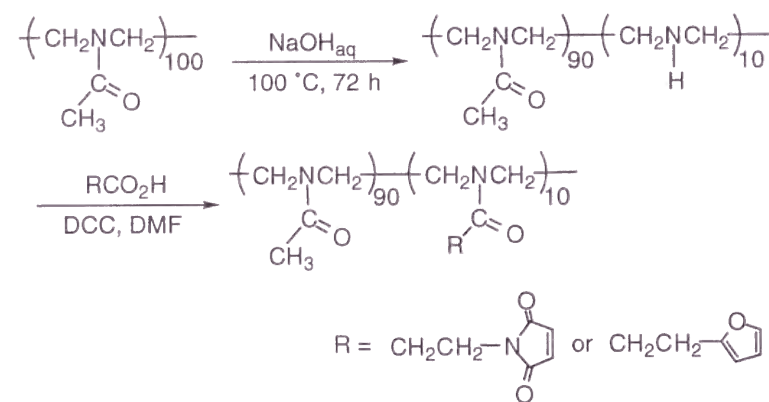
## Experimental Section

### General Procedure

$^1\text{H}$  NMR spectra were recorded using a 270 MHz JEOL-JNM-GX270 NMR spectrometer. IR spectra were obtained using a Perkin Elmer 1600 infrared spectrometer. UV absorption spectra were obtained using a JASCO V-530 spectrophotometer.

### Materials

Maleimide- and furan-modified poly(2-methyl-2-oxazoline)s were prepared according to Scheme 2.<sup>15</sup> Poly(2-methyl-2-oxazoline) of  $M_n \sim 8,500$  (degree of polymerization  $\sim 100$ ) was used as a main chain polymer. The loading levels of each functional group in the polymer were estimated to be 12.4 mol% and 9.4 mol%, respectively, from  $^1\text{H}$  NMR data. Tetramethoxysilane (TMOS) was distilled under nitrogen atmosphere. Methanol was dried with magnesium methoxide and distilled under nitrogen atmosphere. Hydrochloric acid ( $0.1 \text{ mol dm}^{-3}$ ) and DMF were used as supplied.



**Scheme 2.** Preparation of maleimide- and furan-modified poly(2-methyl-2-oxazoline)s.

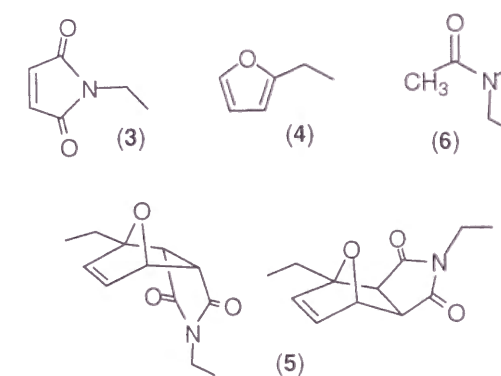
### Preparation of Polymer Hybrids

In a typical experiment, same quantities of polymers **1** and **2** were dissolved in methanol (10 times to TMOS in volume). To the solution, TMOS and hydrochloric acid (4

equivalents to TMOS) were added. The reaction mixture was sealed and stirred at room temperature for a certain period. Then the mixture was placed in a polypropylene mold covered with a paper towel to allow the evaporation of the solvent. A polymer hybrid was obtained as a glassy solid. Films of the polymer hybrids for absorption measurement were prepared by casting the reaction mixture onto quartz substrates.

### Absorption Spectra Analysis

*N*-Ethylmaleimide (**3**) and 2-ethylfuran (**4**) were employed as model compounds. DA adducts (**5**) were prepared from **3** and **4** according to the procedure described previously.<sup>15</sup> Molar absorption coefficients of compounds **3** ~ **5** and *N,N*-diethylacetamide **6** (a model for a monomer unit of the main chain) at wavelength of 296 nm were  $500 \text{ M}^{-1}\text{cm}^{-1}$ ,  $20 \text{ M}^{-1}\text{cm}^{-1}$ ,  $40 \text{ M}^{-1}\text{cm}^{-1}$  (same values were observed for exo and endo isomers), and  $10 \text{ M}^{-1}\text{cm}^{-1}$ , respectively. Efficiencies of the DA reaction in the polymer hybrids were estimated from the absorption at 296 nm by utilizing above values.



**Scheme 3.** Model compounds.

### Solvent Extraction

The powdered hybrids were suspended in DMF and stirred for 1 week, followed by Soxhlet extraction with methanol to achieve complete removal of DMF. The amount of organic components remaining in the hybrids was evaluated by elemental analysis for nitrogen.



## Results and Discussion

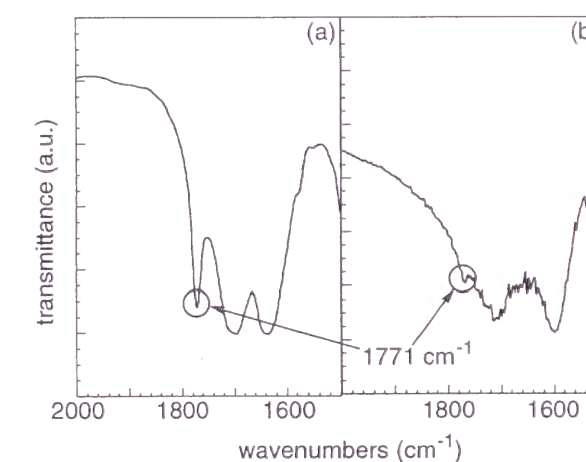
To achieve the thermally reversible formation of organic-inorganic IPN polymer hybrids, polymer hybrids were prepared from maleimide- and furan-modified poly(2-methyl-2-oxazoline)s. Maleimide- and furan-modified poly(2-methyl-2-oxazoline)s were successfully prepared by condensation of partially hydrolyzed poly(2-methyl-2-oxazoline) with the corresponding carboxylic acid derivatives as depicted in Scheme 2. These polymers cross-link in a mixed bulk film by DA reaction between maleimide and furan.<sup>15</sup> The resulting hydrogels do not dissolve but rather swell in water. By heating at 80 °C, the retro-DA reaction takes place, and the degraded hydrogels become soluble.

At first, polymer hybrids were prepared from each polymer via the acid-catalyzed sol-gel reaction of TMOS (Table 1, runs 1 and 2). Both gave transparent and homogeneous polymer hybrids. These polymers were then applied to the preparation of IPN polymer hybrids. The same quantities of polymers **1** and **2** were dissolved in methanol. To the solution was added a certain quantity of TMOS and hydrochloric acid (4 equivalents to TMOS). The resulting mixtures were stirred in sealed bottles for a certain time before allowing the solvent to evaporate in air. It was found that the length of the stirring time had the significant effect on the homogeneity of the resulting polymer hybrids. Too short a stirring time resulted in phase separation of polymer and silica gel (run 3). Homogeneous polymer hybrids could be prepared with stirring times longer than 3 h. To attain the quantitative conversion of TMOS to silica gel, stirring time of 48 h was employed for further preparation of polymer hybrids with different weight ratios of polymer to silicate (runs 6 ~ 8). The weight ratios could be varied widely without affecting the homogeneity of the polymer hybrids. The organic-inorganic compositions of the polymer hybrids were found to be in agreement with the theoretical values.

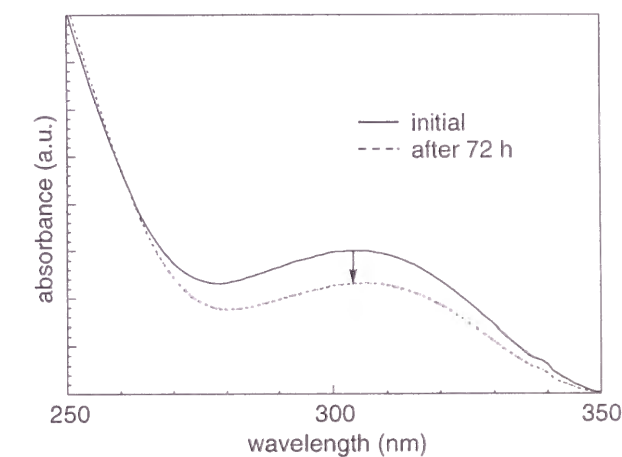
**Table 1.** Preparation and Properties of Polymer Hybrids from Polymers **1** and **2**.

run	polymer <b>1</b> (mg)	polymer <b>2</b> (mg)	TMOS (mg)	stirring time (h)	appearance	polymer content (wt%)	
						calcd.	obsd. <sup>a</sup>
1	100	-	1,000	1	transparent	20.0	14.7
2	-	100	1,000	1	transparent	20.0	14.4
3	50	50	1,000	1	turbid	-	-
4	50	50	1,000	3	transparent	20.0	14.3
5	50	50	1,000	24	transparent	20.0	15.1
6	50	50	250	48	transparent	50.0	45.5
7	100	100	250	48	transparent	66.7	62.8
8	200	200	250	48	transparent	80.0	76.8

<sup>a</sup> Calculated from elemental analysis for nitrogen.



**Figure 1.** FT-IR spectra of (a) compound **5** and (b) polymer hybrid (run 8).



**Figure 2.** UV absorption spectra of polymer hybrid (run 7).



DA reaction of maleimide and furan groups in the polymer hybrids was monitored by FT-IR as well as UV absorption spectroscopy. In the FT-IR spectrum of **5**, a new peak at 1771 cm<sup>-1</sup> specific to DA adducts of maleimides was observed (Figure 1a). This peak appeared on the shoulder of the amide carbonyl peak (Figure 1b) after keeping the polymer hybrid at room temperature for sufficient time, indicating that the DA reaction actually took place in the polymer hybrids.

Quantitative evaluation of the extent of DA reaction was conducted via UV absorption spectra. The films of polymer hybrids were prepared by casting the precursor mixtures onto quartz substrates. After the evaporation of the solvent, the change of UV absorption was followed. It was confirmed by UV spectroscopy that DA reaction in the dilute solution of polymer **1** and **2** was negligible within a few hours. Hence it was assumed that DA reaction hardly took place after 5 minutes from casting. Typical change of the absorption during the reaction can be seen in Figure 2. The decline of the absorption at ca. 300 nm is due to the conversion of maleimide and furan groups to DA adducts. The efficiency of DA reaction was evaluated according to the equation

$$\frac{A_f}{A_i} = \frac{\epsilon_M C_M (1-x) + \epsilon_F C_F (1-x) + \epsilon_{DA} C_M x + \epsilon_A C_A}{\epsilon_M C_M + \epsilon_F C_F + \epsilon_A C_A}$$

where  $A_i$  and  $A_f$  are absorbances at the initial and final, respectively;  $\epsilon$  and  $C$  are molar absorption coefficient and concentration of the chromophore, respectively; subscripts  $M$ ,  $F$ ,  $DA$ , and  $A$  denote the maleimide, furan, DA adducts, and amide unit in the main chain; and  $x$  is the DA extent. As degrees of substitution of both polymers **1** and **2** are about 10 mol%, the relationship  $C_A = 10C_M = 10C_F$  was applied. The DA reaction was found to end within 72 h. The DA efficiencies in each hybrid are listed in Table 2 as well for the pure polymers. In the film composed of polymer **1** and **2**, the DA efficiency was 63%. Lower efficiencies were observed in the polymer hybrids. In polymer hybrids composed of almost the same amount of organic polymer and silica gel (run 6), an efficiency of 27% was still obtained.

Table 2. Properties of Polymer Hybrids.

run	polymer 1/polymer 2/TMOS	DA efficiency (%) <sup>a</sup>	solvent extraction efficiency (%) <sup>b</sup>
1	100/0/1000	-	55
2	0/100/1000	-	61
4	50/50/1000	0	-
5	50/50/1000	0	-
6	50/50/250	27	61
7	100/100/250	30	84
8	200/200/250	47	14
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9	50/50/0	63	-
10	50/50/0 + polyoxazoline 100	36	-

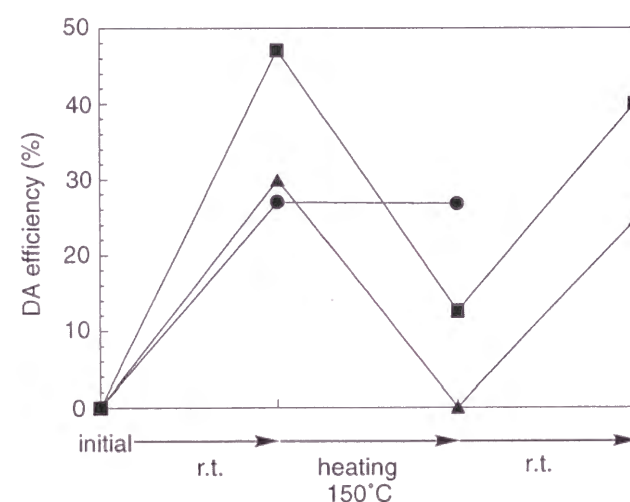
<sup>a</sup> Calculated from UV data. <sup>b</sup> The polymer content of the polymer hybrids before and after the extraction ( $p_b$  and  $p_a$ , respectively) was calculated from elemental analysis for nitrogen, and the solvent extraction efficiency  $E$  was calculated according to the equation :  $E = (p_b - p_a)/(1-p_a)p_b$ .

However, no DA reaction could be detected if the polymer content was too low (runs 4 and 5). When the film of polymer **1** and **2** was diluted with the same amount of poly(2-methyl-2-oxazoline) (run 10), the DA efficiency was diminished to 36%. This suggests that the decrease of DA efficiency in the polymer hybrids can be attributed to the dilution of functional groups with silica gel. These FT-IR and UV spectroscopy data are consistent with the occurrence of DA reaction in the polymer hybrids. The resulting polymer hybrids possess the IPN structure of organic gel and silica gel. As the DA reaction in this system is necessarily an interchain reaction, the DA efficiencies represent the cross-linking density of the organic gel as well.

The modification of solvent resistance by the formation of IPN structure was checked by means of solvent extraction experiments. The organic polymers in powdered polymer hybrids were extracted with DMF, and the portion of organic polymer remaining in the polymer hybrids was estimated. The results are also summarized in Table 2. Improvement of solvent resistance was observed in the polymer hybrids with the highest polymer content

(run 8). The DA reaction efficiency of this polymer hybrid was 47%, indicating that about 5 functional groups react on each polymer chain. Generally speaking, more than 3 or 4 cross-linking points per chain are necessary for gelation of organic polymers. The same trend was found in the present study, thus the critical change of solvent resistance was observed between the number of the cross-linking points of 3 and 5.

The retro-DA reaction in the IPN polymer hybrids was examined by heating the polymer hybrids up to 150 °C and followed by UV absorption spectroscopy. As mentioned previously, the retro-DA reaction in the hydrogel prepared from polymers **1** and **2** took place at 80 °C.<sup>15</sup> In the polymer hybrids, however, a higher temperature was required for the retro-DA reaction. Figure 3 shows the results of retro-DA reaction in the polymer hybrids. In the polymer hybrid (run 6 in Table 1), no change in the UV spectrum was observed. The retro-DA reaction might be suppressed due to the surrounding rigid silica matrix. On the other hand, efficient recovery to maleimide and furan was confirmed in the polymer hybrid having larger polymer contents (runs 7 and 8). Especially, the quantitative retro-DA reaction was achieved in the sample of run 7. Furthermore, when the polymer hybrids were kept at room temperature again, the DA reaction between maleimide and furan groups took place and analogous DA efficiencies were obtained.



**Figure 3.** DA - retro-DA cycles in the polymer hybrids. ● : run 6 ; ▲ : run 7 ; ■ : run 8.

## Conclusion

Thermally reversible formation of IPN structure in the organic-inorganic polymer hybrids was investigated by utilizing the DA reaction between maleimide and furan groups. Transparent and homogeneous polymer hybrids could be obtained by means of acid catalyzed sol-gel reaction of TMOS in the presence of maleimide- and furan-modified poly(2-methyl-2-oxazoline)s. The DA reaction in the polymer hybrids was confirmed by FT-IR and UV absorption spectroscopy. The solvent resistance of the polymer hybrids to leaching could be improved by the formation of an IPN structure via the cross-linking of organic polymer. The retro-DA reaction also takes place in the polymer hybrids, and these reactions could be cycled. Thus thermo-responsive polymer hybrids could be achieved.

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## Chapter 6

### Thermoresponsive Polymer Hybrids from Poly(*N*-isopropylacrylamide)

#### Abstract

Thermoresponsive organic-inorganic polymer hybrids were prepared from *N*-isopropylacrylamide (NIPA), methylenebisacrylamide (BIS), and tetramethoxysilane (TMOS) by the *in-situ* polymerization method. The obtained PNIPA/silica polymer hybrids were examined by porosimetry, swelling degree measurement, and DSC. Samples with BIS content (the mass of BIS per the total mass of the organic component) larger than  $1/_{100}$  showed excellent solvent-resistant property due to their interpenetrating polymer network (IPN) structure. The polymer hybrids swelled in water, and the swelling degree decreased continuously with raising temperature. This behavior was related to an endothermic peak of DSC analysis of the swollen hybrid, which corresponded to the dissociation of the hydrophobic interaction of PNIPA chain.



## Introduction

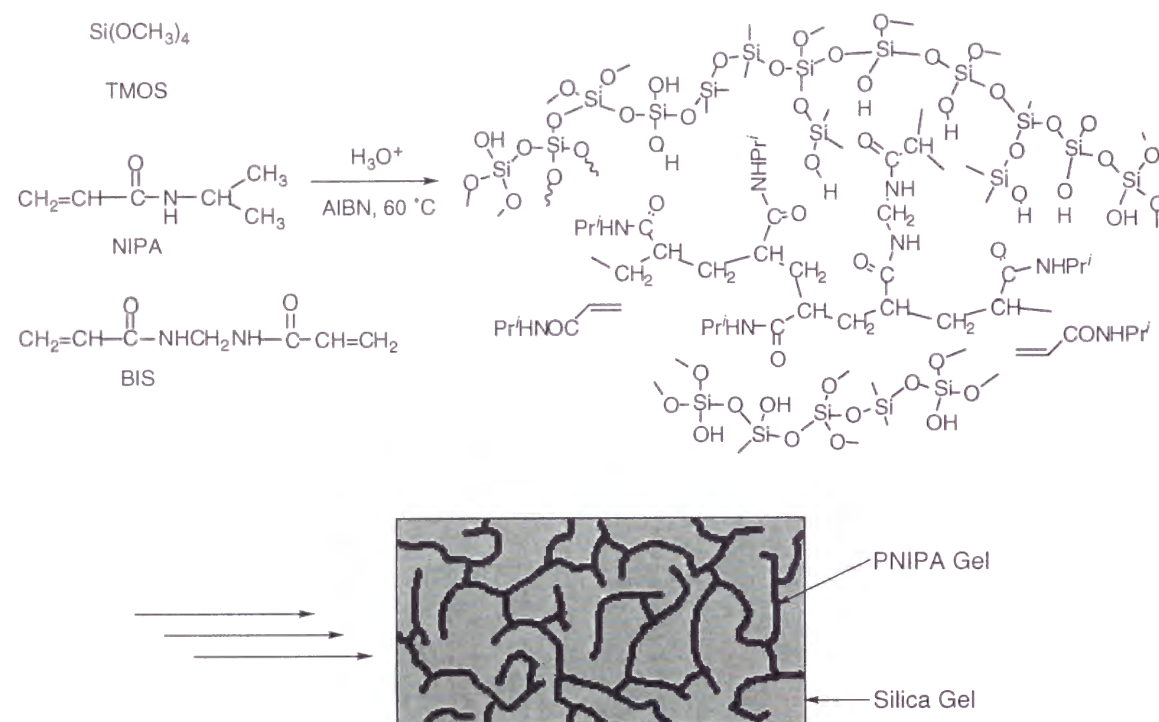
Molecular composites of organic and inorganic compounds have been of great interest as a novel class of materials.<sup>1-3</sup> They potentially serve and surpass the parent materials in properties. The sol-gel technique of alkoxysilanes has been found to be the most convenient means for the preparation of these composite materials. It consists of hydrolysis of the alkoxysilanes and subsequent polycondensation of silanols, and finally a three-dimensional siloxane network can be formed at ambient temperature. During the process, organic materials can coexist and be incorporated into silica gel. A noteworthy feature of the sol-gel reaction is the presence of unreacted silanol groups after the gelation. It allows us to utilize hydrogen bonding interaction to obtain molecular composite materials of organic polymers and silica gel (organic-inorganic polymer hybrids).<sup>4,5</sup> Organic polymers having amide groups in their repeating unit such as poly(2-methyl-2-oxazoline), poly(*N*-vinylpyrrolidone), and poly(*N,N*-dimethylacrylamide) have been incorporated in silica gel homogeneously at the molecular level by adding them into a sol-gel reaction mixture at an initial stage. The formation of hydrogen bond between silanol groups and amide groups was confirmed from FT-IR study. Recently another method for the preparation of the polymer hybrids has been developed.<sup>6-8</sup> Radical copolymerization of organic monomers and the sol-gel reaction of alkoxysilanes were carried out simultaneously *in-situ*. One of the advantages of this "*in-situ* polymerization method" is that by employing multi-functional organic monomers with mono-functional ones, three-dimensional organic gel can be formed in the polymer hybrids. The resulting materials are so-called interpenetrating polymer networks (IPNs) of organic gel and inorganic silica gel, and one can expect high thermal, mechanical, and solvent-resistant properties.

Many researchers have showed particular interests in polymeric materials which change their physical or chemical properties reversibly in response to certain external stimuli (light, heat, pH, and so on) from both scientific and practical points of view. Part I of this thesis demonstrated photoresponsive organic-inorganic polymer hybrids prepared from side-chain functionalized organic polymers. Photoresponsive organic-inorganic polymer hybrids were

prepared from azobenzene-modified poly(2-methyl-2-oxazoline) and reversible trans-cis isomerization of azobenzene was investigated kinetically.<sup>9,10</sup> Photochromic polymer hybrids were prepared from spiropyran-modified poly(*N,N*-dimethylacrylamide).<sup>11</sup> Photodimerization of coumarin groups was utilized to form IPN structure reversibly in the polymer hybrids.<sup>12</sup> The solvent-resistant property was found to be improved by the formation of IPN structure.

Another kind of polymer hybrids which respond to a variation of temperature is presented here. Poly(*N*-isopropylacrylamide) (PNIPA) was employed as a thermoresponsive organic polymer.<sup>13-26</sup> PNIPA has a lower critical solution temperature (LCST) in water and its gel in water undergoes a volume phase transition from swollen to shrunken states at  $T_c$  ( $\approx 34$  °C) when the temperature is raised.<sup>14-18</sup> This is attributed to the hydrophobic interaction between PNIPA and water molecules. There are some examples of PNIPA/silica composite materials. Porous glass grafted with PNIPA altered pore size with temperature owing to thermoresponsive coil-globule conformation change of PNIPA chain.<sup>27,28</sup> PNIPA has also been grafted or adsorbed on silica surface to modify their surface properties from hydrophilic to hydrophobic in response to temperature.<sup>29-31</sup> And molecular composite of PNIPA and silica gel via sol-gel method has been reported by Kurihara et al.<sup>32</sup> In their system, PNIPA domain and silica gel were linked through covalent bond.

This chapter describes the preparation of PNIPA/silica polymer hybrids, where PNIPA (gel) and silica gel are combined without covalent bonding between them. As PNIPA contains amide group in the repeating units, we can expect the hydrogen bonding interaction between PNIPA and silica. Moreover, as NIPA is radically polymerizable monomer, both the traditional and the *in-situ* polymerization methods can be applied. The swelling property to water and thermoresponsive behavior were also investigated.



Scheme 1.

## Experimental Section

### Materials

*N*-Isopropylacrylamide (NIPA) was recrystallized from *n*-hexane. *N,N'*-Methylenebisacrylamide (BIS) was recrystallized from ethanol. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Tetramethoxysilane (TMOS) was distilled and stored under nitrogen atmosphere. Methanol was dried with and distilled from magnesium methoxide, and stored under nitrogen atmosphere. Deionized sterile water (WAKO Pure Chemical Industries, Ltd.) and 0.1 M aqueous hydrochloric acid were used as received.

### Measurements

<sup>1</sup>H-NMR spectra were recorded on a 270MHz JEOL-JNM-GX270 NMR spectrometer.

Differential scanning calorimetry (DSC) thermograms were obtained with a DSC200, Seiko Instruments Inc. Thermogravimetric analysis (TGA) was performed on a Shimadzu TG-30, TGC-30 at the rate of 10 °Cmin<sup>-1</sup> in air. Nitrogen adsorption porosimetry was conducted with BEL JAPAN INC., Nitrogen Adsorption Porosimetry.

### Synthesis of PNIPA/Silica IPN Polymer Hybrids by In-situ Polymerization Method

A typical procedure is as follows. In a 50 ml sample tube, NIPA (1.8 g, 15.9 mmol), BIS (0.20 g, 1.3 mmol), TMOS (1.0 g) and AIBN (29 mg, 0.18 mmol) were dissolved in 10 ml of methanol. To the solution was added 0.25 ml of 0.1 M HCl<sub>aq</sub>. The tube was sealed and the mixture was stirred at room temperature for 3 hours. The cover of the tube was then changed to an aluminum foil with 5 pores (1 mm in diameter). The mixture was then heated at 60 °C under nitrogen atmosphere for 1 week. Polymer hybrid was obtained as a transparent lump.

### Solvent-Resistant Property of Polymer Hybrids

Polymer hybrids were ground in a mortar and the resulting powders were extracted with methanol by using Soxhlet apparatus for 1 week. The quantity of the organic component remaining in the polymer hybrids after extraction was evaluated from elemental analysis of nitrogen.

### Swelling Property of Polymer Hybrids in Water

A piece of the polymer hybrid was swollen in deionized water until the weight of the swollen hybrid no longer changed. Swelling degree was defined as

$$\text{Swelling Degree} = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \quad (\text{eq. 1})$$

where  $W_{\text{wet}}$  is the weight of the swollen hybrid and  $W_{\text{dry}}$  is the weight of the dried hybrid.

### Differential Scanning Calorimetry (DSC)



Polymer hybrid swollen in water was sealed in a seal-type aluminum pan, and DSC thermogram was recorded from 20 °C to 60 °C with the heating rate of 3 °Cmin<sup>-1</sup>.

#### Nitrogen Adsorption Porosimetry

The ground polymer hybrid was calcined at 600 °C for 24 hours under ambient atmosphere to remove organic component. The resulting porous sample was then dried at 200 °C for 2 hours at reduced pressure under nitrogen atmosphere. Surface areas were calculated with the BET equation in the range of 0.05 to 0.30 ( $p/p_0$ ) and the pore size distribution was calculated by BJH method from the desorption curve.

## Results and Discussion

### Synthesis of PNIPA-Silica IPN Polymer Hybrids

Polymer hybrids of PNIPA and silica gel can be prepared by either the traditional and the *in-situ* polymerization methods. As the objective of this study is the investigation of swelling property in water and thermoresponsive behavior of the hybrids, extraction of organic component into water must be suppressed. IPN polymer hybrids are one of the promising candidates. Therefore the preparation of PNIPA/silica polymer hybrids by the *in-situ* method was mainly studied. NIPA, BIS, AIBN, and TMOS were dissolved in methanol and 0.1 M HCl<sub>aq</sub> was added. Then the mixture was stirred at room temperature for 3 hours to make the sol-gel reaction of TMOS take place to some extent. Next the mixture was heated at 60 °C to initiate the radical copolymerization of NIPA and BIS (Scheme 1). It was observed that the reaction proceeded homogeneously and glassy transparent materials were obtained after removal of the solvent. The results of the preparation of PNIPA/silica gel polymer hybrids by the *in-situ* method are summarized in Table 1.

**Table 1.** PNIPA/Silica Gel Polymer Hybrids by the *In-situ* Polymerization Method.<sup>a</sup>

run	TMOS <sup>b</sup> NIPA+BIS	BIS <sup>b</sup> NIPA+BIS	appearance	weight loss (wt%) <sup>c</sup>	unextracted polymer content (wt%) <sup>d</sup>	swelling degree in water
1	1	0	transparent	68	25	-
2	1	1/1000	transparent	68	25	-
3	1	1/100	transparent	62	76	1.18
4	1	1/10	transparent	63	96	1.19
5	1	1/2	turbid	-	-	-
6	2	1/100	transparent	53	82	0.39
7	2	1/10	transparent	51	99	0.53
8	1/2	1/100	transparent	86	85	12.54
9	1/2	1/10	transparent	85	99	4.16

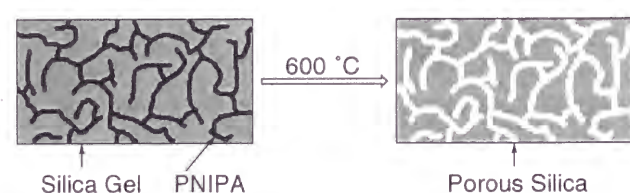
<sup>a</sup> conditions : NIPA + BIS = 2.0 g; AIBN = 1 mol% to total organic monomers; methanol = 20 ml; 0.1 M HCl<sub>aq</sub> = 2 eq. to TMOS. <sup>b</sup> w/w. <sup>c</sup> calculated by TGA. <sup>d</sup> remained polymer content after extraction with methanol, calculated from the results of elemental analysis of nitrogen.

Transparent and homogeneous polymer hybrids were obtained in most cases, except when the content of the crosslink agent BIS (defined as the mass of BIS per the total mass of the organic component) was too high (run 5). The feed ratio of the organic monomers to TMOS could also be varied between 2 and 1/2 without any influence on the homogeneity. The weight loss values calculated by TGA agreed well with the expected polymer contents in the polymer hybrids. This means that the sol-gel reaction of TMOS proceeded quantitatively. The conversion of the organic monomers to polymer was confirmed from the results of <sup>1</sup>H-NMR spectra of extracts from the polymer hybrids with methanol. The olefin protons were not observed at all in low BIS content samples. Organic materials were hardly extracted at higher BIS content. These results suggest an effective conversion of the organic monomers in the sol-gel reaction mixture. Solvent-resistant properties of the hybrids are discussed separately in later section.



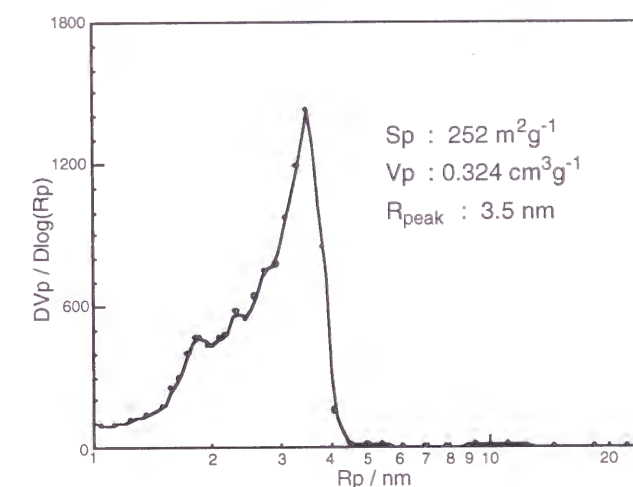
Preparation of polymer hybrids by the traditional method was also examined with preformed PNIPA and TMOS. However, transparent hybrids were obtained only when PNIPA/TMOS ratio was equal to or lower than  $1/_{10}$ . Higher polymer ratio resulted in inhomogeneous hybrids. Improvement of the homogeneity of the polymer hybrids by employing the *in-situ* method was reported in the case of polystyrene/silica gel polymer hybrids.<sup>6</sup> In addition, it is difficult to expect good solvent-resistant property for the traditional polymer hybrids because PNIPA is not crosslinked at all. Therefore further investigation was carried out on the *in-situ* method samples.

Size of organic domain was evaluated by nitrogen adsorption porosimetry of calcined hybrids (Figure 1). Pore size distribution was calculated by BJH method. A typical example is shown for run 6 in Figure 2. Pore size distribution had a maximum at 3.5 nm. This pore size seems somewhat larger than those of POZO/silica or PVP/silica polymer hybrids,<sup>4,5</sup> indicating the tendency of PNIPA to aggregate due to the hydrophobicity of isopropyl groups. No larger pores, however, were observed. This suggests that PNIPA gel and silica gel are combined in the order of nano-meter and the IPN structure is definitely formed.



**Figure 1.** Formation of porous silica gel from a polymer hybrid.

As the amide group of PNIPA is secondary amide and can form hydrogen bonding by themselves, it was difficult to distinguish the formation of hydrogen bonding between amide groups and silanol groups by FT-IR. It can be said at least that the molecular composites of PNIPA and silica having IPN structure were prepared by this method without utilizing covalent bonding between PNIPA and silica.



**Figure 2.** Pore size distribution of calcined PNIPA/silica polymer hybrid (run 6).

#### *Solvent-Resistant Property*

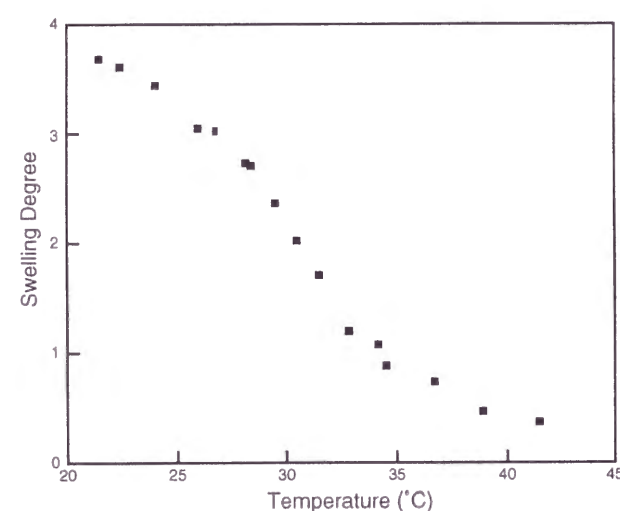
Solvent-resistant property of the PNIPA/silica IPN polymer hybrids was examined by Soxhlet extraction method using methanol. Contents of PNIPA remained in the polymer hybrids were evaluated from the results of elemental analysis of nitrogen (Table 1, 5th column). Most of PNIPA was found to remain after extraction when BIS content was equal to or higher than  $1/_{100}$ , while larger part of the polymer was extracted with lower crosslink densities (runs 1 and 2). In order to investigate the swelling property in water and thermoresponsive behavior of the hybrids, therefore BIS content equal to or higher than  $1/_{100}$  is necessary to have enough solvent-resistant property.

#### *Thermoresponsive Swelling Behavior to Water*

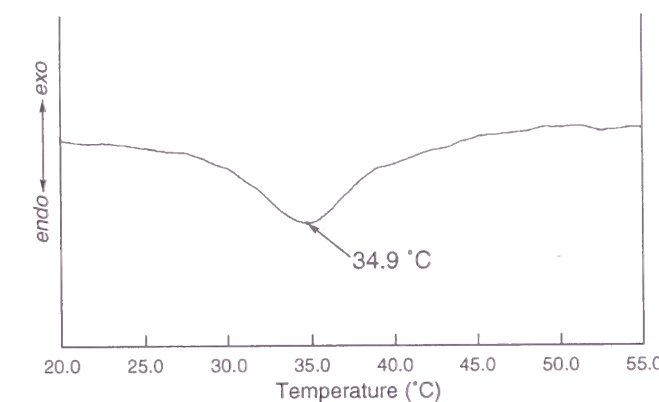
Swelling degrees of the hybrids in water at temperature lower than 20 °C are also summarized in Table 1. A piece of the polymer hybrid of about 2 mm thick and 5 mm in diameter was swollen in deionized water until the weight of the swollen hybrid no longer changed. Equilibrium of the swelling was achieved within 2 days. The highest swelling

degree (defined in eq. 1) was obtained in run 8 to be 12.54, and the swelling degree was found to decrease with increasing BIS content (run 9). The swelling degrees also decreased with lower organic content, but these hybrids still absorbed water of almost same weight with themselves in runs 3 and 4. It seems that the BIS content didn't affect the swelling degrees of these hybrids. Organic-inorganic ratio was found to be a decisive factor in these low organic content samples.

Temperature dependence of the swelling degree is demonstrated for run 9 in Figure 3. The swelling degree was measured after immersing the samples in water until equilibrium was achieved at various temperatures. The swelling degree decreased continuously with raising temperature. Figure 4 shows the DSC thermogram of PNIPA/silica hybrid (run 9) swollen in water. A clear endotherm was resolved, and the maximum endothermic point at 34.9 °C was chosen as the phase-transition temperature. This temperature is almost the same with the value observed for PNIPA gel.<sup>15,19</sup> This endothermic peak corresponds to the dissociation of the hydrophobic interaction,<sup>15,16</sup> and the temperature dependence of the swelling is closely related to this.



**Figure 3.** Temperature dependence of the swelling degree of PNIPA/silica IPN polymer hybrid (run 9).



**Figure 4.** DSC thermograms of PNIPA/silica IPN polymer hybrid swollen in water (run 9).

## Conclusion

PNIPA/silica IPN polymer hybrids were prepared by the *in-situ* polymerization method and analyzed by porosimetry, swelling degree measurement, and DSC. Organic-inorganic ratio and BIS content could be varied without any influence on the homogeneity of the polymer hybrids. Solvent-resistant property was examined by the Soxhlet extraction method using methanol. BIS content higher than  $1/100$  was enough to prevent the extraction of PNIPA. PNIPA/silica polymer hybrids were swollen in water. The swelling degree was found to depend on organic-inorganic ratio and BIS content. It was found that the swelling degree decreased continuously with raising temperature. This behavior could be related to the dissociation of the hydrophobic interaction of PNIPA chain, which was obvious from the result of DSC thermogram of the swollen hybrid. Mechanical properties of these PNIPA/silica gel polymer hybrids are of interest.

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## Part III

### Polarity-Responsive Organic-Inorganic Polymer Hybrids



## Chapter 7

### Solvatochromic Characterization of Organic-Inorganic Polymer Hybrids with Pyridinium *N*-Phenolate Betaine Dyes

#### Abstract

The local polarity in organic-inorganic polymer hybrids was estimated by employing solvatochromic pyridinium *N*-phenolate betaine dyes. Solvatochromic polymer was prepared by introducing Reichardt's betaine dye in the side chain of poly(2-methyl-2-oxazoline), and the model compound for the dye unit was also prepared. Polymer hybrids were prepared from these compounds and mixtures of various proportions of tetramethoxysilane (TMOS) and methyltrimethoxysilane (MeTMOS). The electronic absorption spectra were measured by the diffuse reflectance method. It was found that the local polarity in the polymer hybrids was affected by the TMOS:MeTMOS ratio and also by the presence of the organic polymer. And it was suggested that the dye molecules are preferentially surrounded by the organic polymer than the siloxane network in the polymer hybrids.

## Introduction

Sol-gel derived organic-inorganic nanocomposites have received a great amount of scientific and technological interests during past 2 decades.<sup>1-5</sup> Ambient processing condition of the sol-gel technique enable one to construct nanocomposites of organic and inorganic components.<sup>6</sup> Several types of preparation methods have been proposed for the organic-inorganic nanocomposites. Organically-modified silica gels (ormocers) were prepared by the sol-gel reaction of alkoxysilanes having organic residues (e.g., methyltrimethoxysilane or phenyltrimethoxysilane).<sup>7,8</sup> Alkoxysilanes having polymerizable functional group such as methacryl group can polymerize with both organic monomers such as methyl methacrylate (MMA) and inorganic precursors, resulting the hybrid material where organic polymer and inorganic network are linked covalently.<sup>7,8</sup> Impregnation of MMA to the porous silica gel and subsequent radical polymerization of MMA afford another kind of organic-inorganic composite matrix.<sup>9</sup> Organic polymers are coexisted in the sol-gel reaction of alkoxysilanes to construct organic-inorganic hybrid matrices.<sup>10,11</sup>

It is of great interest to utilize these nanocomposites as host media for numerous organic, organometallic, and biological molecules.<sup>12-17</sup> This approach has been applied extensively for the design and synthesis of a wide range of novel materials in the fields of photonics (solid-state dye lasers,<sup>18-20</sup> nonlinear optics,<sup>21-23</sup> optical storage,<sup>24</sup> optical switches<sup>25</sup>), sensors,<sup>26,27</sup> and biological catalysts.<sup>28</sup> Probing the microenvironment of the entrapped molecules in the nanocomposites is another interest.<sup>15,29-35</sup> The nature of the local environment around the entrapped molecule is usually decisive to achieve the desired property. It is necessary to understand the microenvironment around the doped molecules to predict and design the property of the molecules and the resulting property of the materials.

Solvatochromic techniques for characterizing the local polarity around the dye have been developed.<sup>36-38</sup> The techniques are based on the solvent-dependent shifts of absorption band of a dye used as a probe for the solvation properties of a given medium. Polarity is one of the most important properties of such materials, as the property of the doped molecule are

intrinsically affected by their surroundings. Here, "solvent polarity" is the overall solvation capability of the solvents.<sup>37</sup> Reichardt's betaine dye (2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate) is well-known solvatochromic dye and frequently used to determine the polarity of the medium experimentally.<sup>36,37</sup> It exhibits a quite large negative solvatochromism, and the polarity of the medium is estimated by the molar electronic transition energy of a dye,  $E_T$ , as defined by eq. 1.

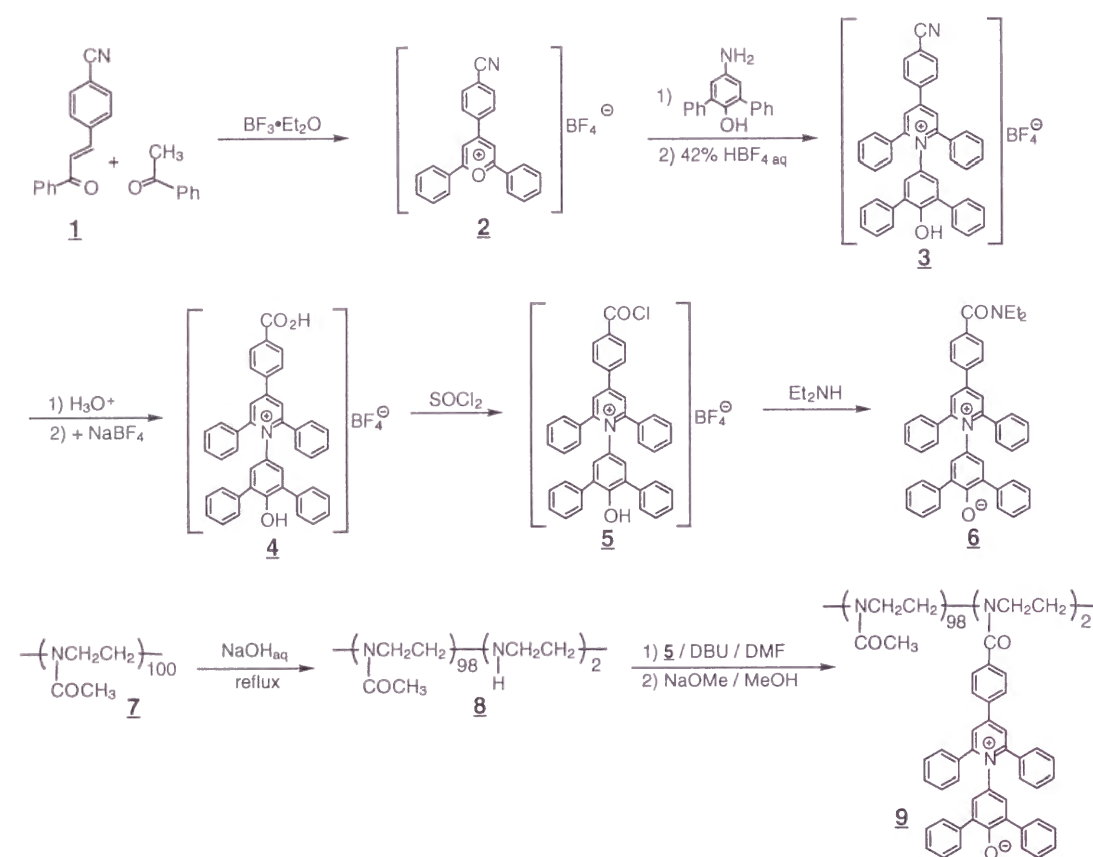
$$E_T (\text{kcal mol}^{-1}) = hcN_A \nu_{\max} = 28,591/\lambda_{\max} (\text{nm}) \quad (\text{eq. 1})$$

Here  $h$  is Plank's constant,  $c$  is the speed of light in a vacuum,  $N_A$  is Avogadro's number, and  $\nu_{\max}$  and  $\lambda_{\max}$  are the frequency and the wavelength of the absorption maximum of the intramolecular charge-transfer band of the dye. A high  $E_T$  value corresponds to high solvent polarity.  $E_T$  value for Reichardt's betaine dye has been utilized as an empirical scale for solvent polarity and called  $E_T(30)$ -scale. This scale was also utilized to investigate the polarity of solid matrix such as organic polymers or sol-gel glass.<sup>32,39</sup>

Chujo *et al.* have been investigating the organic-inorganic polymer hybrids, which are the molecular composite materials of organic polymers and a three-dimensional siloxane network.<sup>10,11</sup> They are prepared by the sol-gel reaction of alkoxysilanes in the presence of organic polymers such as poly(2-methyl-2-oxazoline) and poly(*N*-vinylpyrrolidone). The hydrogen-bonding interactions between amide groups of the organic polymers and silanol groups remaining in the siloxane network prevent the aggregation of the organic polymer during the sol-gel reaction and induce the molecular level homogeneity.

In this chapter, the local polarity of microenvironment in the organic-inorganic polymer hybrids was investigated by utilizing the solvatochromic method. The solvatochromic polymer was prepared by incorporating Reichardt's betaine dye in the side chain of poly(2-methyl-2-oxazoline) (polymer **9** in Scheme 1), and the model compound for the dye unit was also synthesized (compound **6** in Scheme 1). They were coexisted in the sol-gel reaction of

TMOS and MeTMOS. The local polarity was estimated and compared with each other.



**Scheme 1.** Synthesis of solvatochromic polymer **9** and model compound **6**.

## Experimental Section

### Materials

Preparation of poly(2-methyl-2-oxazoline) (**7**) and partial hydrolysis of amide groups of polymer **7** to obtain copolymer **8** were reported previously.<sup>40</sup> Distilled reagents were stored under nitrogen atmosphere. Acetophenone and boron trifluoride diethyl etherate were distilled under reduced pressure. Chloroform was dried and distilled from CaH<sub>2</sub>. Acetone was dried and distilled from K<sub>2</sub>CO<sub>3</sub>. Diethylamine was distilled. DMF was dried and distilled from MgSO<sub>4</sub> under reduced pressure. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was distilled under reduced pressure. 4-Cyanobenzaldehyde, 4-amino-2,6-diphenylphenol,

42% aqueous tetrafluoroboric acid, sodium tetrafluoroborate, concentrated aqueous hydrochloric acid, glacial acetic acid, thionyl chloride, and sodium methoxide were used as received. Tetramethoxysilane (TMOS) and methyltrimethoxysilane (MeTMOS) were distilled.

### Measurements

<sup>1</sup>H NMR spectra were recorded on a 270 MHz JEOL-JNM-GX270 NMR spectrometer. <sup>13</sup>C NMR spectra were recorded on a 67.5 MHz JEOL-JNM-GX270 NMR spectrometer. IR spectra were obtained on a Perkin Elmer 1600 infrared spectrometer. UV/VIS/NIR absorption spectra of solutions and films were obtained on a JASCO V-530 spectrophotometer. Diffuse reflectance UV/VIS/NIR absorption spectra of polymer hybrids were obtained on a Perkin Elmer UV/VIS/NIR spectrometer Lambda 19 attached with a Labsphere RSA-PE-19 reflectance spectroscopy accessory. Thermogravimetric analysis (TGA) was performed on a Shimadzu TG-30, TGC-30 with the heating rate of 10 °Cmin<sup>-1</sup> up to 950 °C under air. Nitrogen adsorption porosimetry was conducted on a BEL JAPAN INC. The powdered polymer hybrid was calcined at 600 °C in air for 24 h to remove organic components. The resulting porous silica was then dried at 200 °C for 2 h under reduced pressure before porosimetry measurement. The surface area was calculated with the Brunauer-Emmett-Teller (BET) equation in the range of 0.05 to 0.30 (p/p<sub>0</sub>) and the pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method.

### 3-(4-Cyanophenyl)-1-phenyl-2-propen-1-one (**1**)

Compound **1** was prepared according to the literature.<sup>41</sup> Yield after recrystallization from ethanol was 75 %.

### 4-(4-Cyanophenyl)-2,6-diphenylpyrylium tetrafluoroborate (**2**)

To a solution of **1** (9.54 g, 40.9 mmol) and acetophenone (2.45 g, 20.4 mmol)<sup>42</sup> in chloroform (50 ml) was added BF<sub>3</sub>·OEt<sub>2</sub> (21 ml) under nitrogen atmosphere. The mixture



was stirred at 60 °C for 50 h. Diethyl ether (50 ml) was added and the precipitate was filtered and dried. The crude product was recrystallized from methanol to give 2.96 g (35 %) of **2** as a yellow crystal. Mp., <sup>1</sup>H NMR, and IR were in agreement with the data in the literature.<sup>41</sup> <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>) : 118.06, 118.64, 118.82, 130.46, 130.59, 131.50, 131.72, 134.83, 137.02, 138.58, 166.20, 177.35.

*4-(4-Cyanophenyl)-1-(4-hydroxy-3,5-diphenylphenyl)-2,6-diphenylpyridinium tetrafluoroborate (3)*

Compound **3** was prepared according to the literature.<sup>41</sup> Yield after recrystallization from *i*-propanol was 76 %.

*4-(4-Carboxyphenyl)-1-(4-hydroxy-3,5-diphenylphenyl)-2,6-diphenylpyridinium tetrafluoroborate (4)*

The procedure in the literature 41 was slightly modified. Compound **3** (1.14 g, 1.71 mmol) in a mixture of conc. Hydrochloric acid (100 ml), glacial acetic acid (60 ml), and water (33 ml) was refluxed for 90 min. After cooling to room temperature, 30% aqueous NaBF<sub>4</sub> (75ml) was added and left overnight in a refrigerator. The precipitate was filtered, washed well with water, recrystallized from water-methanol, and dried at 60 °C under reduced pressure. Compound **4** was obtained as a yellow crystal (76%). Mp., <sup>1</sup>H NMR, and IR were in agreement with the data in the literature.<sup>41</sup>

*2,6-Diphenyl-4-{[4-(4-*N,N*-diethylcarbamoylphenyl)-2,6-diphenyl]-*N*-pyridino} phenolate (6)*

Compound **4** (144 mg, 0.21 mmol) was refluxed with thionyl chloride (5 ml) for 30 min and then excess thionyl chloride was removed by evaporation. Acyl chloride **5** was used to the next step without further purification. In dried acetone (5 mL) was dissolved **5** under nitrogen atmosphere and diethylamine (74 mg, 1.0 mmol) was added dropwisely with stirring. The resulting deep-purple mixture was stirred at room temperature for 30 min before removing

the solvent by evaporation. The remaining solid was washed well with water and dried at 80 °C under reduced pressure. Dye molecule **6** was obtained as a deep green solid. Yield was 100 mg (0.15 mmol, 75 %). <sup>1</sup>H NMR (CD<sub>3</sub>OD) : δ 1.15 and 1.28 (broad peaks, 6H, CH<sub>3</sub>), 3.33 and 3.58 (broad peaks, 4H, CH<sub>2</sub>), 6.82 (s, 2H, 3,5-positions of phenolate), 7.08 - 7.58 (m, 20H, Ph), 7.63 and 8.21 (AB system, *J*<sub>AB</sub> = 8.3 Hz, 4H, aromatic protons of 4-carbamoylphenyl ring), 8.47 (s, 2H, aromatic protons of pyridinium ring). <sup>13</sup>C NMR (CD<sub>3</sub>OD) : δ 13.84 and 15.19 (CH<sub>3</sub>), 41.73 and 45.69 (CH<sub>2</sub>), 127.82, 128.02, 128.34, 128.63, 129.48, 129.57, 130.41, 130.73, 131.27, 131.78, 132.01, 133.59, 136.18, 137.24, 141.41, 142.36, 157.15, 159.63, 162.11, 172.98 (CO). IR (KBr) : 1618 cm<sup>-1</sup> (ν<sub>CO</sub>). Elemental Analysis : Calc. C 80.69, H 5.89, N 4.30 ; Obs. C 80.69, H 5.68, N 4.30.

*Reichardt's Dye-Modified Poly(2-methyl-2-oxazoline) (9)*

Compound **4** (146 mg, 0.21 mmol) was refluxed with thionyl chloride (5 ml) for 30 min and then excess thionyl chloride was removed by evaporation. Acyl chloride **5** was used to the next step without further purification. Acyl chloride **5** and 2 mol%-hydrolyzed poly(2-methyl-2-oxazoline) **8** (470 mg, 0.10 mmol NH) were dissolved in DMF (10 ml) under nitrogen atmosphere and DBU (15 mg, 0.10 mmol) was added to trap HCl gas. The mixture was stirred at room temperature overnight. The polymer was isolated by reprecipitation into diethyl ether and further purified by reprecipitation from methanol into diethyl ether (two times). The resulting precursor polymer was dissolved in methanol (10 ml) and sodium methoxide (18 mg, 0.3 mmol) in methanol (5 ml) was added. The color of solution turned deep purple, and the solution was stirred for 10 minutes. The polymer was isolated by reprecipitation from methanol into diethyl ether (4 times) and freeze-dried with benzene. Yield was 443 mg (92 %). Quantitative introduction of the chromophore on the polymer chain and complete conversion to phenolate by the treatment with sodium methoxide was confirmed by <sup>1</sup>H NMR as well as electronic absorption spectroscopies. In the <sup>1</sup>H NMR spectrum of polymer **9** in CD<sub>3</sub>OD, the methylene protons next to secondary amine groups in

polymer **8** disappeared and peaks of aromatic protons corresponding to the chromophore appeared in the same position of the model compound **6**. Solvatochromic behavior of polymer **9** in various solvents is discussed later.

#### Preparation of Polymer Hybrids and Sol-Gel Glasses from Solvatochromic Compounds

In a typical experiment a mixture of 100 mg of polymer **9**, 0.20 ml of TMOS, 0.19 ml of MeTMOS (molar ratio of 5:5), and 2 ml of methanol was sonicated for 10 min, then 0.17 ml of water was added, followed by sonication for additional 10 min. The mixture was placed in a polypropylene mold covered with a paper towel, and left in air at room temperature for 5 days and then at 60 °C for 2 days. The obtained solid was ground in a mortar, and the resulting powder was heated at 120 °C for 12 h to complete the sol-gel reaction. The polymer hybrids from model compound **6** and polyoxazoline **7** were prepared in the same way as above, with employing 100 mg of polyoxazoline **7** and 13.6 mg of compound **6** instead of polymer **9**. The model **6**-doped sol-gel glasses were prepared similarly, but without polymer.

#### Electronic Absorption Spectra

All the solvents for measurement of absorption spectra were dried and distilled in traditional methods according to the literature.<sup>43</sup> The concentration of the dye was set to be ca.  $3 \times 10^{-4}$  M to acquire absorbances of the intramolecular charge-transfer band  $\approx 1$ . A film of polymer **9** was prepared by casting methanol solution onto a quartz substrate followed by drying *in vacuo* at 110 °C for 3 h. A film of model **6**-doped polyoxazoline was prepared by casting methanol solution (3 mg of model **6** and 100 mg of polymer in 0.5 mL of methanol) onto a quartz substrate followed by drying *in vacuo* at 110 °C for 3 h. The spectra of the films were obtained by using a clean quartz substrate of same thickness as the reference. The diffuse reflectance absorption spectra of the powdered polymer hybrids were obtained by using MgO<sub>2</sub> powder as the reference. The powders of polymer hybrids were dried *in vacuo* at 120 °C just before the measurement.

### Results and Discussion

The solvatochromic polymer **9** and its model compound **6** were prepared according to Scheme 1. The degree of introduction of the dye into the polymer was calculated to be 2 mol% from the <sup>1</sup>H NMR spectrum, which was in good agreement with the degree of hydrolysis of the precursor polymer **8**. Quantitative introduction of the chromophore on the polymer chain was also confirmed by the disappearance of methylene protons adjacent to secondary amine group in **9**. Aromatic peaks of **9** corresponded well with those of **6**, indicating that the betaine dye was actually formed in the side chain of the polymer.

The electronic absorption spectra of **6** were observed in various solvents. The absorption maximum wavelength ( $\lambda_{\max}$ ) of the intramolecular charge-transfer band shifted from 781 nm (in THF) to 531 nm (in methanol). The polarity parameter  $E_T$  values in each solvents are listed in Table 1. Table 1 also includes  $E_T$  values of **9** and Reichardt's dye.<sup>37</sup> Because of the low solubility of polymer **9** especially in nonpolar solvents, only 4 solvents were examined for polymer **9**. Linear correlations between  $E_T$  values of Reichardt's dye and those of **6** or **9** were found to be excellent (Figure 1).

$$E_T(\mathbf{6}) = 0.908 + 0.954E_T(30) ; \text{correlation coefficient } |r| = 0.998$$

$$E_T(\mathbf{9}) = 5.042 + 0.892E_T(30) ; \text{correlation coefficient } |r| = 1.000$$

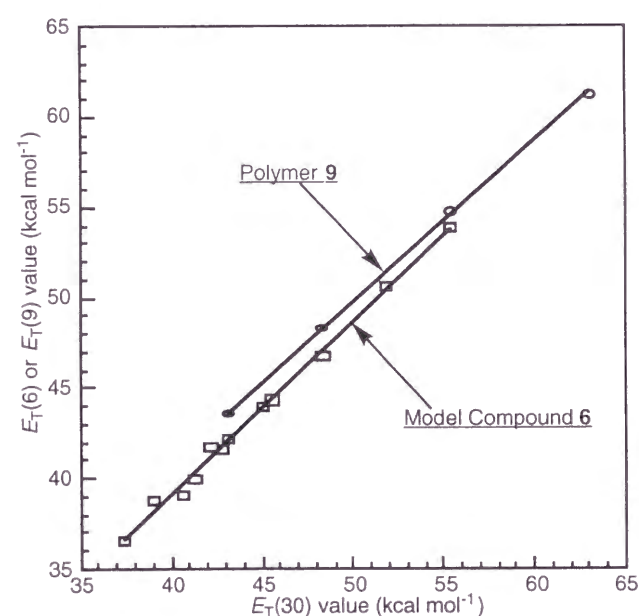
The slopes of the correlation functions indicate slightly lower but comparable solvatochromic sensitivities of these compounds with Reichardt's dye.

The organic-inorganic polymer hybrids were prepared from the polymer **9** with mixtures of various proportions of tetramethoxysilane (TMOS) and methyltrimethoxysilane (MeTMOS) (Table 2). No acid catalyst was used in this study since the protonated phenol form of the chromophore showed no solvatochromism. The polymer hybrids from **6**, polyoxazoline **7** and TMOS/MeTMOS mixture, and **6**-doped TMOS/MeTMOS sol-gel glasses were also prepared. Transparent and homogeneous polymer hybrids were obtained with the molar ratio

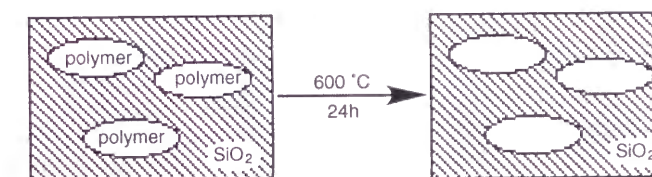


**Table 1.**  $E_T$  values<sup>a</sup> of model compound **6**, polymer **9**, and Reichardt's dye in various solvents.

solvent	model <b>6</b>	polymer <b>9</b>	Reichardt's dye <sup>b</sup>
water	-	61.2	63.1
methanol	53.8	54.7	55.4
ethanol	50.6	-	51.9
2-propanol	46.8	48.2	48.4
acetonitrile	44.3	-	45.6
DMSO	43.9	-	45.1
DMF	42.2	43.5	43.2
DMAc	41.6	-	42.9
acetone	41.7	-	42.2
ClCH <sub>2</sub> CH <sub>2</sub> Cl	40.0	-	41.3
CH <sub>2</sub> Cl <sub>2</sub>	39.1	-	40.7
chloroform	38.8	-	39.1
THF	36.6	-	37.4

<sup>a</sup> In kcal mol<sup>-1</sup>. <sup>b</sup> From ref. 37.**Figure 1.** Correlations between the  $E_T$  values of **6** or **9** and those of Reichardt's dye in various solvents**Table 2.** The results of preparation and  $E_T$  values of polymer hybrids and sol-gel glasses from polymer **9** and model **6**.

TMOS : MeTMOS (molar ratio)	Polymer <b>9</b>			Model <b>6</b> + polyoxazoline		Model <b>6</b>	Reichardt's dye <sup>b</sup>
	appearance	ceramics yield <sup>a</sup> (%)	$E_T$ ( <b>9</b> ) (kcal mol <sup>-1</sup> )	ceramics yield <sup>a</sup> (%)	$E_T$ ( <b>6</b> ) (kcal mol <sup>-1</sup> )	$E_T$ ( <b>6</b> ) (kcal mol <sup>-1</sup> )	$E_T$ (30) (kcal mol <sup>-1</sup> )
5 : 5	transparent	98	47.1	83	45.9	50.5	47.0
6 : 4	transparent	97	47.4	88	46.1	53.6	49.3
7 : 3	transparent	98	47.8	88	46.4	53.8	50.2
8 : 2	transparent	101	48.5	90	46.9	56.2	54.1

<sup>a</sup> Ceramics yield = (wt% of ceramics in polymer hybrids observed by TGA) / (calculated value of wt% of ceramics).<sup>b</sup> From ref. 32.**Scheme 2.** Formation of porous silica from the polymer hybrid by calcination.**Table 3.** Porosity of Calcined Polymer Hybrids.<sup>a</sup>

TMOS : MeTMOS (molar ratio)	$S_{BET}$ <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	$R_{peak}$ <sup>c</sup> (nm)
8 : 2	222	1.8
7 : 3	218	1.9
6 : 4	205	1.8
5 : 5	179	1.8

<sup>a</sup> The porous silica was obtained by charring the polymer hybrid at 600 °C for 24 h. <sup>b</sup> Surface area calculated by BET method. <sup>c</sup> Pore radius calculated by BJH method from desorption branch.

of TMOS:MeTMOS from 8:2 to 5:5. The quantitative progress of the sol-gel reaction of



TMOS and MeTMOS was confirmed by thermogravimetric analyses (TGA) of the obtained polymer hybrids. The dispersity of organic polymers in the polymer hybrids was evaluated by nitrogen adsorption porosimetry. The polymer hybrids were calcined at 600 °C for 24 h to achieve complete removal of organic components (Scheme 2). The siloxane lattice is so rigid that it would not be affected at this temperature. Therefore, the size of the remaining pores was expected to be comparable to the size of the domain of organic polymer. Surface areas as well as pore radii evaluated by nitrogen adsorption porosimetry are listed in Table 3. All the porous silica gels prepared from the polymer hybrids had the surface area of ca. 200 m<sup>2</sup>g<sup>-1</sup> and the sharp pore size distributions peaked at 1.8 - 1.9 nm. These results suggest the nano-level dispersion of the organic polymer in the polymer hybrids.

The electronic absorption spectra of the polymer hybrids and the sol-gel glasses were observed by diffuse reflectance absorption spectroscopy. Representative spectra for **9**/TMOS/MeTMOS and **6**/7/TMOS/MeTMOS were shown in Figure 2. The absorption bands in the polymer hybrids were found to be somewhat broader than those in methanol solution, indicating the heterogeneity of matrix in the solid polymer hybrid compared with the solution phase. However, as suggested from the results of nitrogen adsorption porosimetry, the organic polymers were dispersed in the range of a few nanometers. The polarity of matrices could be estimated from the maximum wavelength of the absorption. The  $E_T$  values are collected in Table 2. It was found that the  $E_T$  values became larger with higher TMOS ratio in all cases and were linearly correlated with the relative amounts of TMOS (Figure 3). The linear correlations ( $|r| > 0.985$ ) denote a homogeneous polymerization of TMOS and MeTMOS.

Moreover, it is noticed that there is a remarkable difference between the polymer hybrids and the sol-gel glasses, in other words, between the samples containing organic polymer and those without polymer. In the polymer hybrids, the change of  $E_T$  values with different TMOS:MeTMOS ratio, and consequently the slopes of the correlation functions in Figure 3, diminished compared with those of the sol-gel glasses. The model compound **6**-doped sol-gel glasses exhibited almost the same change toward TMOS:MeTMOS ratio as

Reichardt's dye-doped ones. On the contrary, the polymer hybrids from the polymer **9** and those from polyoxazoline **7** and the model **6** appeared to show smaller changes of  $1/5$  or  $1/6$ .

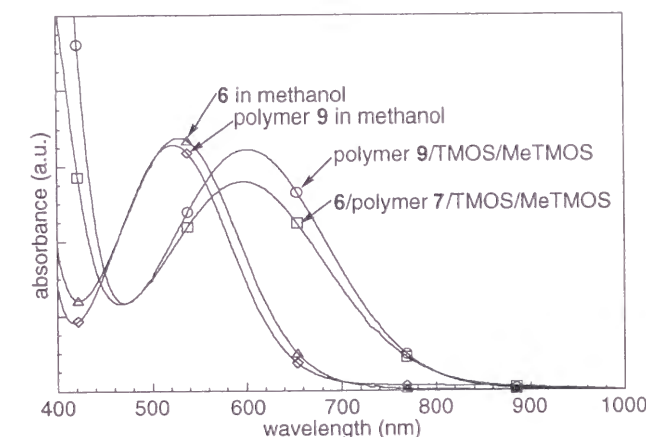


Figure 2. Representative absorption spectra.

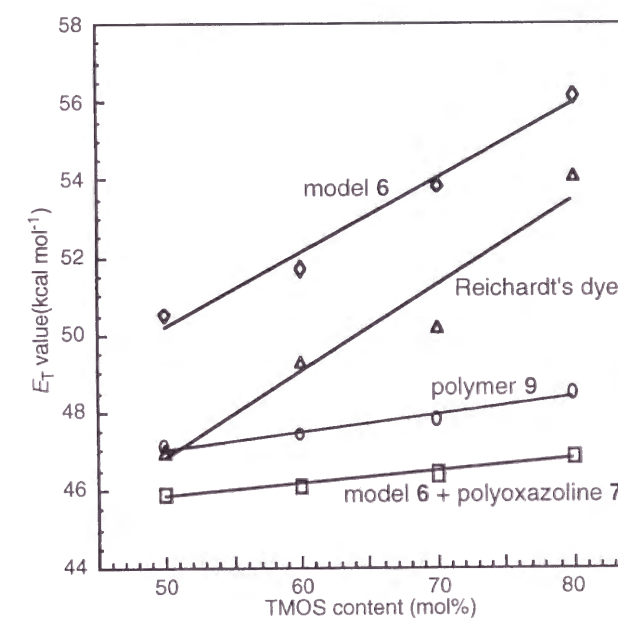
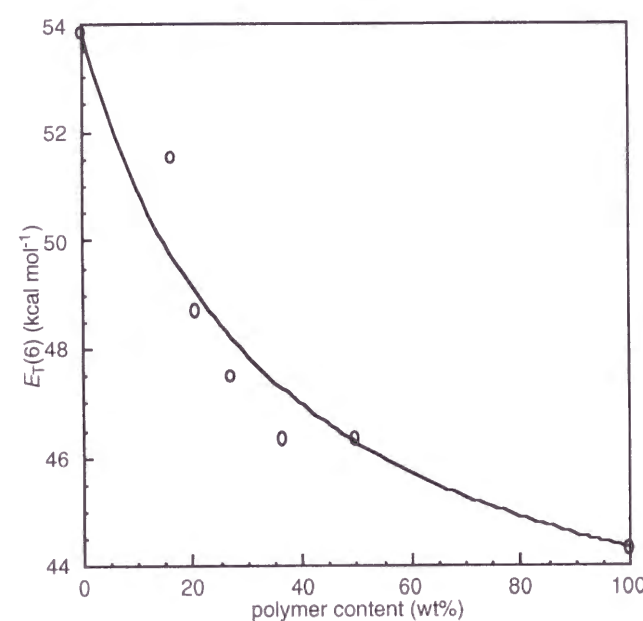


Figure 3. Matrix polarity as a function of the molar percent of TMOS.

As mentioned above, the solvatochromic sensitivities of **6** and **9** are comparable to that of

Reichardt's dye in solution (Figure 1), and indeed **6** doped in the sol-gel glasses showed a large difference of the  $E_T$  values with different TMOS:MeTMOS ratios. Therefore the decline of solvatochromic changes in the polymer hybrids should be attributed to the presence of the organic polymer in the solid state. The solvatochromic dye seems to experience a more polymer-like environment but is substantially influenced by the sol-gel matrix.<sup>30</sup>

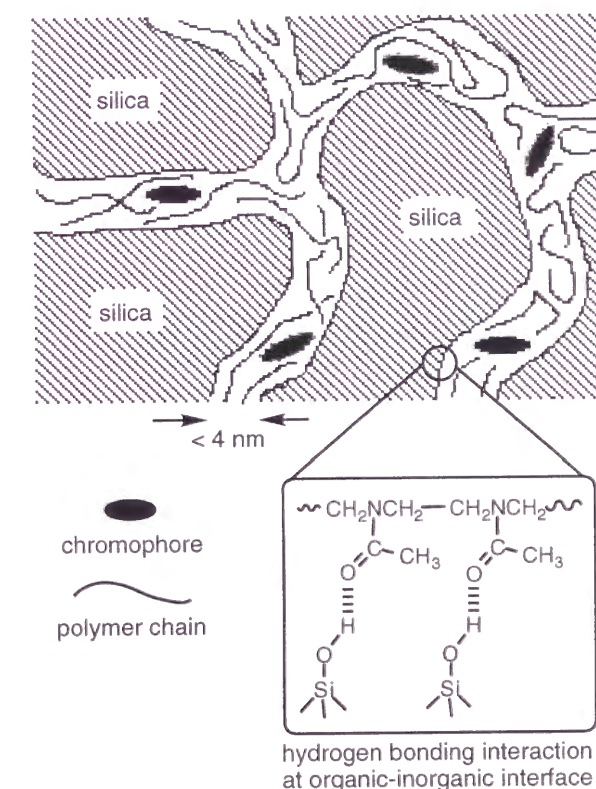
In order to verify this circumstance, **6**-doped polymer hybrids with different polymer/silicate ratios (TMOS:MeTMOS = 7:3) were prepared and those absorption spectra were measured. In Figure 4, the obtained  $E_T$  values are plotted against the polymer content (wt%) determined from TGA measurements. It again suggests that the microenvironment around the dye **6** composed of a larger amount of organic polymer than the bulk composition. This kind of phenomena is frequently observed in binary solvent mixtures and described as "preferential solvation".<sup>36,44</sup> Figure 5 presents a simple illustration consistent with the microenvironment felt by the solvatochromic dye in the polymer hybrids.



**Figure 4.** Matrix polarity of model **6**/polyoxazoline **7**/TMOS:MeTMOS(7:3) polymer hybrids as a function of polymer content in wt%

At present it is not clear whether the concentration fluctuation of organic polymer

exists in the polymer hybrids and the doped dye molecule is located in the polymer-rich environment or the doping of the dye molecule induces the concentration fluctuation. It can also be pointed out that the slopes of the linear correlation lines for the polymer hybrids in Figure 3 are almost the same. This indicates that the polarity of the microenvironments around the dye are apparently equivalent independently of the existence of chemical bond between the dye and the polymer.



**Figure 5.** Illustration representing the dispersion of the chromophore in a polymer hybrid.



## Conclusion

The polarity of the microenvironment in the organic-inorganic polymer hybrids was characterized with the solvatochromic pyridinium *N*-phenolate betaine dyes. The solvatochromic parameter  $E_T$  values of the polymer hybrids were found to correlate linearly with TMOS:MeTMOS ratio. It seems that the solvatochromic dyes are preferably surrounded by the organic polymer than the siloxane network in the polymer hybrids. Furthermore, the polarity of the microenvironments around the dye molecule are apparently equivalent whether the dye is chemically connected to organic polymer or not. These results suggest the possibility of more precise control of the property of the dye molecule doped in the polymer hybrids by controlling the microenvironment around the dye.

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## **List of Publications**

## List of Publications

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- Chapter 1. Imai, Y.; Naka, K.; Chujo, Y. *Macromolecules* **1998**, *31*(2), 532-534.  
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- Chapter 5. Imai, Y.; Itoh, H.; Naka, K.; Chujo, Y. *Macromolecule* **2000**, in press.
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